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RENOVATION OF INDUSTRIAL INORGANIC WASTEWATER BY EVAPORATION WITH INTERFACE ENHANCEMENT

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Industrial feasibility demonstration projects for each of the three wastewater types examined are recommended. A method and flow diagram for the desalination-recycle of power plant cooling tower blowdown by interface-enhanced VTE integrated with typical power plant coolant cycle and utilizing waste heat from that cycle, is described and recommended.

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RENOVATION OF INDUSTRIAL INORGANIC WASTEWATER BY EVAPORATION WITH INTERFACE ENHANCEMENT

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FOREWORD

The multi-media character of pollution resulting from the extraction, processing, conversion, and utilization of energy and mineral resources, and from industrial processing and manufacturing, requires an approach which recognizes the complex impact of these operations on our environment.

The Industrial Environmental Research Laboratory, Cincinnati, utilizes a multidisciplinary approach in the development and demonstration of technologies to effectively deal with the pollution associated with these operations. The Laboratory assesses the environmental and socio-economic impact of industrial and energy-related activities and identifies and evaluates control alternatives.

This report evaluates a novel method of increasing the efficiency of an evaporative process to recycle three types of industrial waste waters; power plant cooling tower blowdown, industrial steam generation blowdown, and an acidic mine drainage type of wastewater. The method, known as interface enhancement, involves the addition of a surfactant to the wastewater stream prior to passing the stream through a vertical tube evaporator. For all three waste streams a considerable increase in heat transfer performance was observed. It was concluded that substantial capitol and operating cost savings could be realized by modifying existing evaporation systems to accommodate the interface enhancement technique.

This project was one of several projects undertaken by IERL-C to demonstrate new approaches to increasing the reuse of industrial wastewater, a source of much water pollution throughout the country. This report will be especially interesting to those individuals involved in the design or operation of industrial systems which use large amounts of water for cooling purposes, and to individuals involved in industrial waste water research.

David G. Stephan
Director
Industrial Environmental Research Laboratory,Cincinnati

ABSTRACT

A novel method of vertical tube evaporation (VTE) to improve heat transfer performance was applied to the concentration of three types of industrial wastewaters. This method, interface enhancement*, relies upon the addition of a few parts per million of a selected surfactant to the wastewater feed followed by imposed two-phase foamy liquid-vapor flow over the heat transfer surfaces. Applied to the concentration of power plant cooling tower blowdown and boiler blowdown, interface-enhanced VTE provided an approximate 120 percent increase in the usual VTE heat transfer performance, using a 5,000 gpd pilot plant having double-fluted aluminum-brass distillation tubes, under process conditions that are realistic for large industrial plants. Acidic mine drainage water, concentrated by double-fluted titanium evaporator tubes provided about a 60 percent heat transfer performance enhancement. Beneficial side effects of the surfactant additive were to inhibit the crystallization of solutes, permitting concentration of the wastewaters to smaller volumes. This work indicates feasibility and improved economics for renovation-recycle of each of the three types of wastewater examined.

Industrial feasibility demonstration projects for each of the three wastewater types examined are recommended. A method and flow diagram for the desalination-recycle of power plant cooling tower blowdown by interface-enhanced VTE integrated with a typical power plant coolant cycle and utilizing waste heat from that cycle, is described and recommended.

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SECTION I: CONCLUSIONS

The following conclusions were drawn from or confirmed by the work reported here:

1) The interface-enhanced mode of operating a vertical tube evaporator (VTE) is technically feasible for the concentration-recycle of each of the three types of industrial wastewaters examined; the main beneficial effects to be anticipated are substantial capital and/or operating cost savings. Evaporator heat transfer performance enhancements ranging from 60 to 150 percent were demonstrated under process conditions that are realistic for industrial operation.

2) Side effects of the interface-enhancement agent examined provided additional advantages; these side effects are an inhibition of the onset of crystal formation during the gradual concentration of wastewater and the dispersant effect of the surfactant additive.

3) In the case of the concentration-renovation of Mohave Power Plant cooling tower blowdown, a tenfold evaporation was readily obtained after the addition of 10 ppm of a selected surfactant, at heat transfer performance rates about double those obtained without the additive. These results indicate that cooling tower blowdown can be most economically desalted for recycle by integrating a VTE loop within the temperature span available in the coolant cycle of a large power plant, as shown in the flow diagram of Figure II.

4) Several alternative methods of cooling tower blowdown renovation-recycle can benefit significantly from the adoption of the interface-enhanced mode of operating an evaporator. These include concentration of blowdown by vapor compression VTE, by multiple effect VTE with upflow or downflow of the feed, and by low temperature VTE utilizing waste heat for evaporation.

5) In the case of examining an industrial boiler blowdown the application of interface-enhanced VTE provided substantial benefits; the evaporator heat transfer performance was more than double its conventional performance, and a concentration factor of 20 was readily obtainable without significant precipitation of solutes occurring.

6) The renovation-recycle of industrial boiler blowdown by either the single effect vapor compression VTE method or by a multiple effect VTE is feasible and appears economically acceptable with the interface-enhanced mode of operation.

7) In the case of the acidic mine drainage type of wastewater examined it was apparent that the addition of a surfactant before its concentration by upflow VTE provides the benefits of retaining particulates in suspension, inhibiting the crystallization of solutes, and of increasing the evaporator heat transfer performance substantially. Because of the highly corrosive nature of this type of effluent, titanium tubes and stainless steel equipment are indicated to be advisable; copper-based alloys were indicated as unsuitable. The heat transfer performance of titanium distillation tubes was increased by about 60 percent by the addition to the feed of about 10 ppm of a selected surfactant.

SECTION II: RECOMMENDATIONS

The following recommendations are submitted, based on the work performed under this project:

1) In order to demonstrate the advantages of this approach for industrial wastewater renovation-recycle to the satisfaction of all interests, a mobile pilot plant facility should be designed in cooperation with an architect-engineering firm knowledgeable in the power plant field. Subsequent field demonstration tests should be jointly sponsored by several interested utilities and carried out in collaboration with such interests, to provide a means for the rapid evaluation and possible adoption of these procedures by industry.

2) Regarding industrial boiler blowdown renovation, it is recommended that a demonstration project be undertaken by a large industrial complex, for instance a petroleum refinery. The objective of such a project would be to design, construct and field test a vapor compression VTE plant of a size and scope that will satisfy industry and the EPA about the application, cost and benefits of the interface-enhanced mode of VTE operation for industrial wastewater recycle.

3) In regard to the concentration and recycle of highly corrosive effluents, such as acid mine drainage and plating plant effluents, it is recommended that further definitive test data be obtained by means of a relatively small (about 3 to 5,000 gpd) mobile vapor compression VTE, constructed of titanium and stainless steel, and tested on three typical wastewaters.

4) The beneficial interface-enhanced heat transfer effects have now been well demonstrated on several types of aqueous media. However, the effects of surfactant additives on evaporation under crystallizing or precipitation

VTE conditions have not been adequately defined. It is recommended that further study be carried out in this area in the interest of wastewater renovation-recycle.

5) The side effects of the surfactant additives that have been identified appear to be beneficial. These are the dispersant effect, the inhibition of solute cyrstallization during concentration, and the inhibition of erosion and corrosion. These side effects should be more precisely defined, especially the longterm benefits and disadvantages, including the useful lifetime of the surfactant additives during continuous recycle and the fate of their thermal degradation products.

SECTION III

INTERFACE-ENHANCED VERTICAL TUBE EVAPORATION

INTRODUCTION

The objective of this project was to obtain heat transfer performance data on the application of a novel evaporative procedure for wastewater renovation by pilot plant tests with several industrial wastewaters. These data would provide a basis for evaluating the process feasibility, and the cost reductions available in the possible future industrial application of this procedure.

The novel distillation method, "Interface Enhancement Applied to the Evaporation of Liquids," (1) relies upon the addition of a few parts per million (ppm) of a selected surfactant to the liquid to be evaporated, followed by imposing foamy two-phase, vapor-liquid flow over the heat transfer surfaces. This mode of flow provides a 4- to 6-fold increase in the brineside or evaporation-side coefficient, which in turn provides an evaporator performance enhancement or overall heat transfer coefficient increase of 50 to 200 percent, for multieffect vertical tube evaporation (VTE) performed under otherwise conventional process conditions (1). The degree of enhancement depends on the process conditions applied, such as whether the upflow or downflow VTE mode is used, the type of distillation tube installed, and the evaporation temperature and the temperature difference applied as well as the type and concentration of surfactant additive used (2, 3, 4, 5). In the case of upflow VTE, the application of interface enhancement has a very significant further effect of improving the upflow tubeside hydrodynamic stability. This follows from the improved foamy mode of flow, whereby the liquid holdup in the distillation tube is reduced by about a factor of 5. Stated differently, the liquid residence time is substantially reduced; this means that the

hydrostatic pressure drop, contributing a parasitic loss, is much reduced. The net result is that the tubeside hydrodynamic pressure gradient is substantially lowered, usually by a factor ranging from 3 to 6. Consequently, the upflow process stability is significantly improved; this in turn permits stable upflow VTE operation at reduced effect-to-effect temperature differences, in the interest of saving heat, or fuel (6, 7). It also permits relatively high heat transfer performance at low evaporation temperatures and under relatively low temperature differences (ΔT); such as used in vapor compression VTE.

Another distinct advantage of the interface-enhanced mode of VTE operation, especially meaningful for wastewater renovation, is that the surfactant additive tends to suppress crystallization of solutes, disperses particulates present in the distilland to prevent their deposition on heat transfer surfaces, and that it can provide some erosion-corrosion protection by the formation of a surfactant layer adsorbed to the heat transfer surface and other surfaces (8).

The planned scope of work included pilot plant tests with three typical industrial wastewaters; test data were to be obtained under typical upflow VTE process conditions including data with the interface-enhanced mode of operation. The wastewaters tested were power plant cooling tower blowdown, industrial steam generator (boiler) blowdown and an acidic mine drainage type.

The pilot plant used was available from the author's earlier OSW-sponsored projects on the development of enhanced heat transfer for VTE of seawater. Some modifications were made for the tests reported here. In addition a small Pyrex glass-tubed upflow VTE was constructed to determine the effect of surfactant additives on solute crystallization during the gradual concentration of these wastewaters.

BACKGROUND

The interface-enhanced mode of upflow VTE had been fairly well defined in previous work in this laboratory, at least for seawater conversion under typical multieffect process conditions (1, 2, 3, 4, 5). Several reports have also appeared on work done elsewhere, confirming the effectiveness of this enhancement procedure for downflow VTE (9) and for horizontal tube multieffect evaporation (HTME) (10).

Approximately four years of development work by pilot plant testing in this laboratory preceeded the present work. During this development period, the interface enhancement effects were defined for a series of special and commercial grade full-sized distillation tubes of both smooth-walled, and various fluted-wall configurations. The process conditions applied included all the most significant parameters imposed in the individual effects of a real, industrial installation. Heat transfer performance enhancement effects had been demonstrated to be consistently obtained with a series of about twelve different surfactants and with both freshwater and seawater feeds under all of the usual range of upflow VTE process conditions (3, 5, 6). The magnitude of this enhancement effect varied in a consistent manner, depending upon the type of distillation tube, the type and concentration of surfactant used and the process conditions applied within the usual multi-effect VTE range. Thus it was known that the most effective upflow VTE performance enhancement effects were obtained when the feed entering the distillation tubes was caused to flash or partially vaporize into a two-phase liquid-vapor flow, for instance, by passing a preheated feed through a suitable nozzle or orifice (3). In this manner evaporation of the liquid is assured to occur along the entire length of the distillation tube.

The most significant interface enhancement effects have been shown to be the following (3, 5):

1) The imposed foamy mode of vapor-liquid flow over the heat transfer surfaces provides for thin-film, wiped-film evaporation. This results from the continuous renewal of the liquid film laid down onto this surface from liquid phase carried interstitially to the vapor bubbles as a network of foam swept over this surface by the vapor phase flow. This thin-film evaporation mechanism applies to both upflow and downflow of the feed. It is important, for high interface enhancement, that the foamy layer be maintained throughout the length of the distillation tubes. This requires initiation of foamy flow as or before the feed enters these tubes, for instance, by flashdown at an orifice; continuation of the foamy layer flow depends on an adequate rate of evaporation, yet a not excessive rate of vapor flow which tends to break the foam up. These parameters determine the diameter and length of distillation tube of a particular metal and flute profile best suited a given evaporation temperature and ΔT applied.

2) The second enhancement effect applies to the upflow VTE mode only. It has been shown that the residence time of the liquid phase (feed) is substantially reduced as a result of the imposed foamy vapor-liquid flow through the tubes. Stated in other words, the liquid hold-up is reduced, and this follows from the more rapid passage of the liquid phase through the tubes as a result of the foamy consistency. As a consequence of this reduced liquid hold-up, the hydrostatic pressure drop axially through the distillation tubes is substantially reduced. This in turn provides for the 3- to 10-fold hydrodynamic tubeside pressure drop reductions. These actual two-phase pressure drops are constituted of a hydrostatic element, and a hydrodynamic element which include accelerational and frictional pressure drop elements. Since the

downflow VTE has a very low hydrodynamic pressure drop and no hydrostatic pressure drop element, the pressure drop reduction effect of interface enhancement does not apply to this mode of VTE. This explains, in part, why interface enhancement is about 50 percent less effective in downflow VTE applications. Another reason is that stable, foamy two-phase flow is much more readily maintained in upflow VTE than in the downflow mode, and at much lower surfactant concentrations.

One of the main additional advantages of interface-enhanced upflow VTE over the downflow application follows from the fact that the former operation does not require effect-to-effect feed transfer or recirculation pumps. This provides a significant capital cost saving and more significant operation-maintenance (O & M) cost savings. A recent cost comparison study performed by Kaiser Engineers (11) concluded that the capital cost savings provided by interface-enhanced upflow VTE over the conventional downflow mode amount to at least 25 percent and that O & M cost savings would be about 30 percent.

The most significant single effect of interface enhancement is to improve the upflow VTE tubeside stability; this permits stable operation even at relatively low ΔT-values. As a consequence, one can increase the number of effects permissible within the available temperature span of 120 to 250°F usually available for a multieffect VTE plant. As a direct result of the increased number of effects, the gain ratio, or economy ratio, is increased by up to 50 percent in the interest of saving steam or fuel. Another result is that design flexibility is improved, allowing improved optimization of capital versus energy costs (4).

Apart from process development knowledge and experience, a 5,000 gallon per day (gpd) upflow VTE pilot plant was available in this laboratory from previous projects sponsored by the Office of Saline Water (OSW), for use in the present study.

PROJECT PLAN

a) An initial phase of about three months was planned during which time the available equipment and facilities were to be reconditioned and improved, in preparation for the main phase of the work. Some preliminary exploratory work would also be done during this phase. Equipment and facilities made available for this project from California State and OSW sources were inventoried at about $75,000.

b) The main phase of this study included definitive tests, with the 5,000 gpd pilot plant, on typical wastewaters evaporated under realistic upflow VTE multieffect process conditions, both without and with surfactant additives to these feeds. It was anticipated that at least three typical industrial wastewaters would be examined. These waters would be selected in collaboration with EPA staff, or as suggested by EPA, to ensure relevance of the test data.

The main benefits to be expected from this project were:

a) A substantial reduction in the cost of renovating industrial wastewaters by VTE, which produces a high quality distilled water for beneficial use. The dispersing effects of surfactant additives, to prevent fouling and scaling of heat transfer surfaces, were to be evaluated. This should permit evaporation to increased solute concentrations, and the evaporation of wastewaters that contain particulate and colloidal matter. Disposal of these relatively small residual concentrates would be at reduced cost;

b) A broadened scope for applying evaporation processes in the renovation of industrial wastewaters, to advance the state of the art of pollution abatement. A recent study by Kaiser Engineers (6) concluded that capital cost savings of about 25 percent and annual cost savings of about 33 percent are obtainable on a 12.5 MGD downflow VTE/MSF plant if an upflow VTE/MSF process with interface enhancement is adopted instead of the downflow mode.

c) Advancement of our understanding of the mechanisms responsible for the substantial increase in heat and mass transfer rates, obtained by the interface enhancement method of evaporation to be applied in this work.

Additional benefits anticipated included training of students while working toward their MS or PhD degrees. Well-trained personnel should provide a valuable service to the public, in the environmental and public utility fields. The proposed project would also be of benefit to the University of California, by providing opportunities and facilities for furthering the educational process, generating innovations and advancing the state of the art in the field of wastewater renovation.

The legal requirements for industrial compliance with water quality standards place a high priority on the rapid development of suitable technology for purification of wastewater. The interface enhancement method for VTE operation of this proposal appeared to provide a very promising tool for complying with these requirements in some instances. Its development, and introduction into this field seemed well justified.

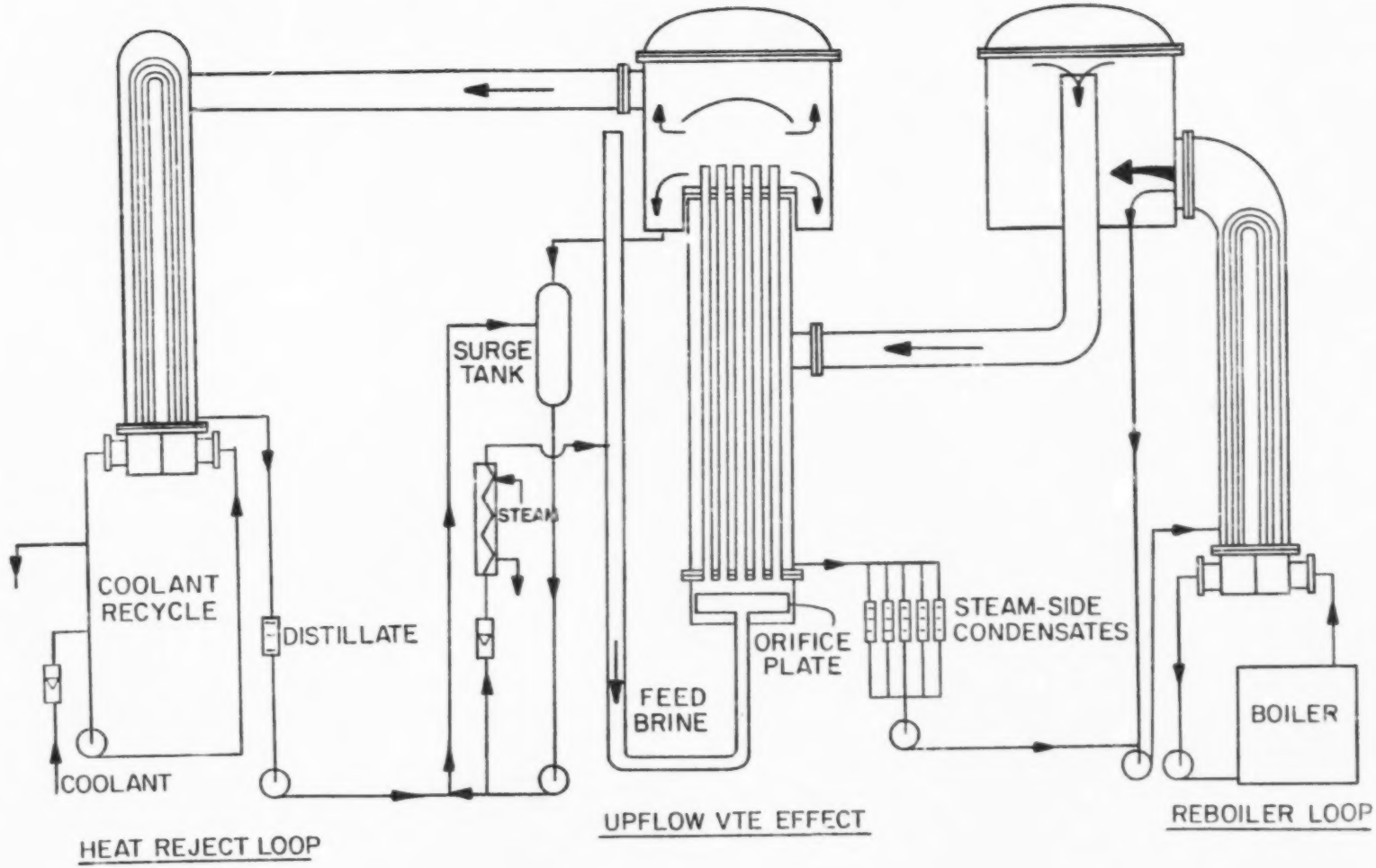
Surfactant Additive Recovery-Recycle

A method of recovery from concentrated brine and recycle of 95-97 percent of the surfactant, added as a heat transfer enhancement agent in the VTE, has been developed through the pilot plant stage[4,5]. This procedure, foam fractionation, provides simultaneous benefits such as removing (and allowing recovery) of metal ions of interest as well as particulates, notably ferric hydroxide from the VTE blowdown concentrate. The foam fractionation procedure is economically attractive.

UPFLOW VTE PILOT PLANT FACILITY USED FOR THIS STUDY

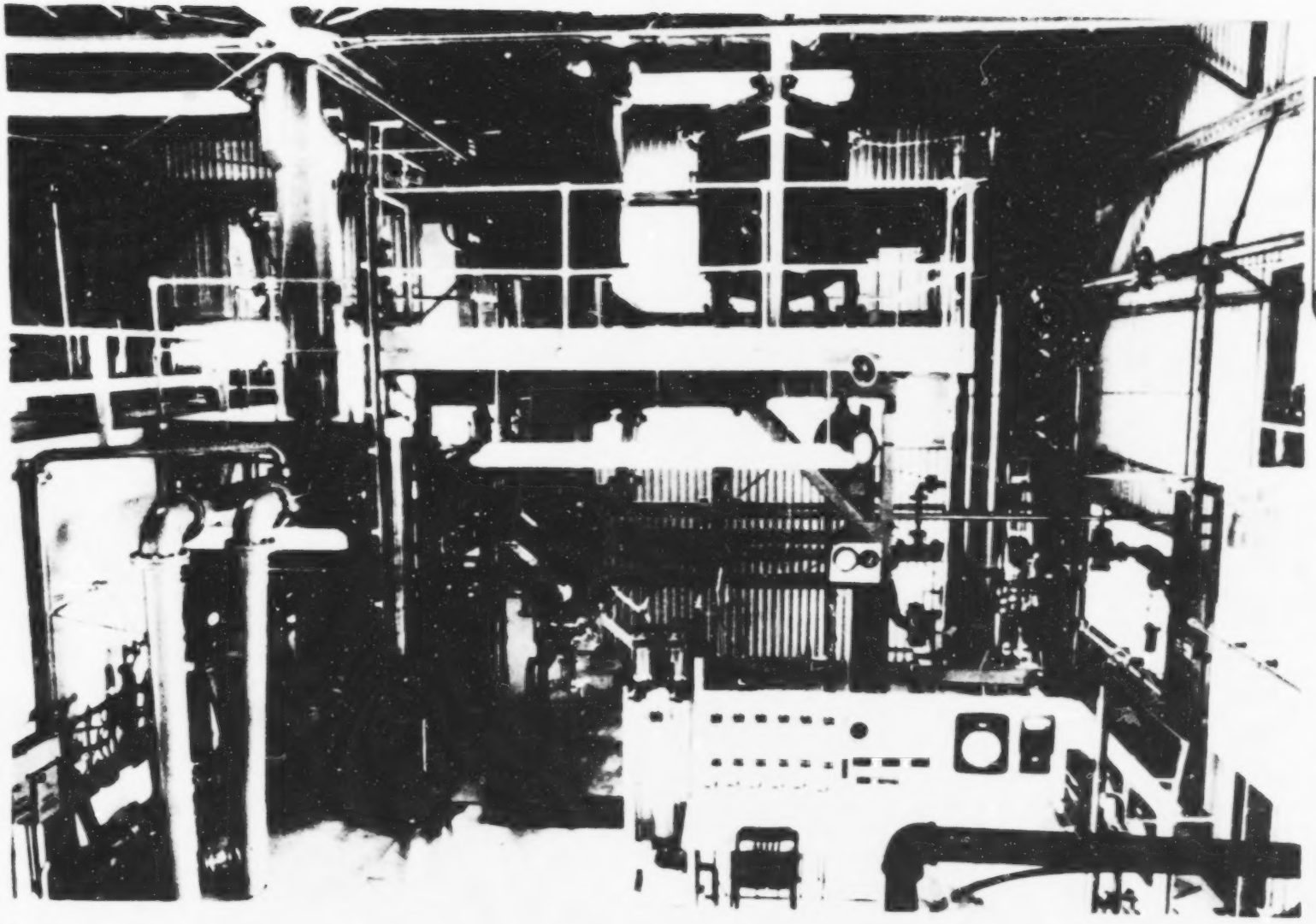
A versatile single effect, 5,000 U.S. gpd, 18-tube VTE pilot plant was designed and constructed primarily with OSW support under earlier research and development projects for application of interface enhancement to seawater desalting (4). This pilot plant was also utilized in this EPA-sponsored work,and is represented in the simplified flow diagram of Figure 1 and shown photographed in Figure 2. This facility, comprising a reboiler loop, an 18-tube VTE loop and a heat reject loop, could impose all the significant process conditions, relevant to any one of the effects in a typical multi-effect VTE plant, upon the 18-tube VTE loop. This loop was constructed from nonferrous materials compatible with wastewater. The tubes used for these tests were double-fluted aluminum-brass (Yorkshire Imperial Metals Ltd.) of 0.042-inch wall thickness, 2-inch OD x 10-foot heated length, in an oxidized-annealed condition. The industrial wastewater tested was recirculated through the VTE loop. The interface-enhanced data were obtained after the further addition of a selected surfactant to the feed in 5 to 50 ppm concentration. The VTE loop was washed with fresh water and charged a fresh batch of wastewater before each test series.

In operation, the desired steam-side temperature (Ts) was preset on an automatic controller actuating a motorized steam valve to admit boiler steam (at 45 psig) to the tubes of the U-tube heat exchanger in the reboiler loop, shown on the far right of Figure 1. Fresh water was evaporated on the shell-side of this heat exchanger while in upflow, two-phase flow. This two-phase stream was injected tangentially into the large-domed vapor release vessel on the upper right of Figure 1. The residual liquid phase was recirculated while the vapor produced was conveyed to the VTE loop to serve as heating steam for the 18-tube bundle. To determine the total heat flux (Q) of the



SIMPLIFIED FLOW DIAGRAM FOR UPFLOW VTE PILOT PLANT

FIGURE 1



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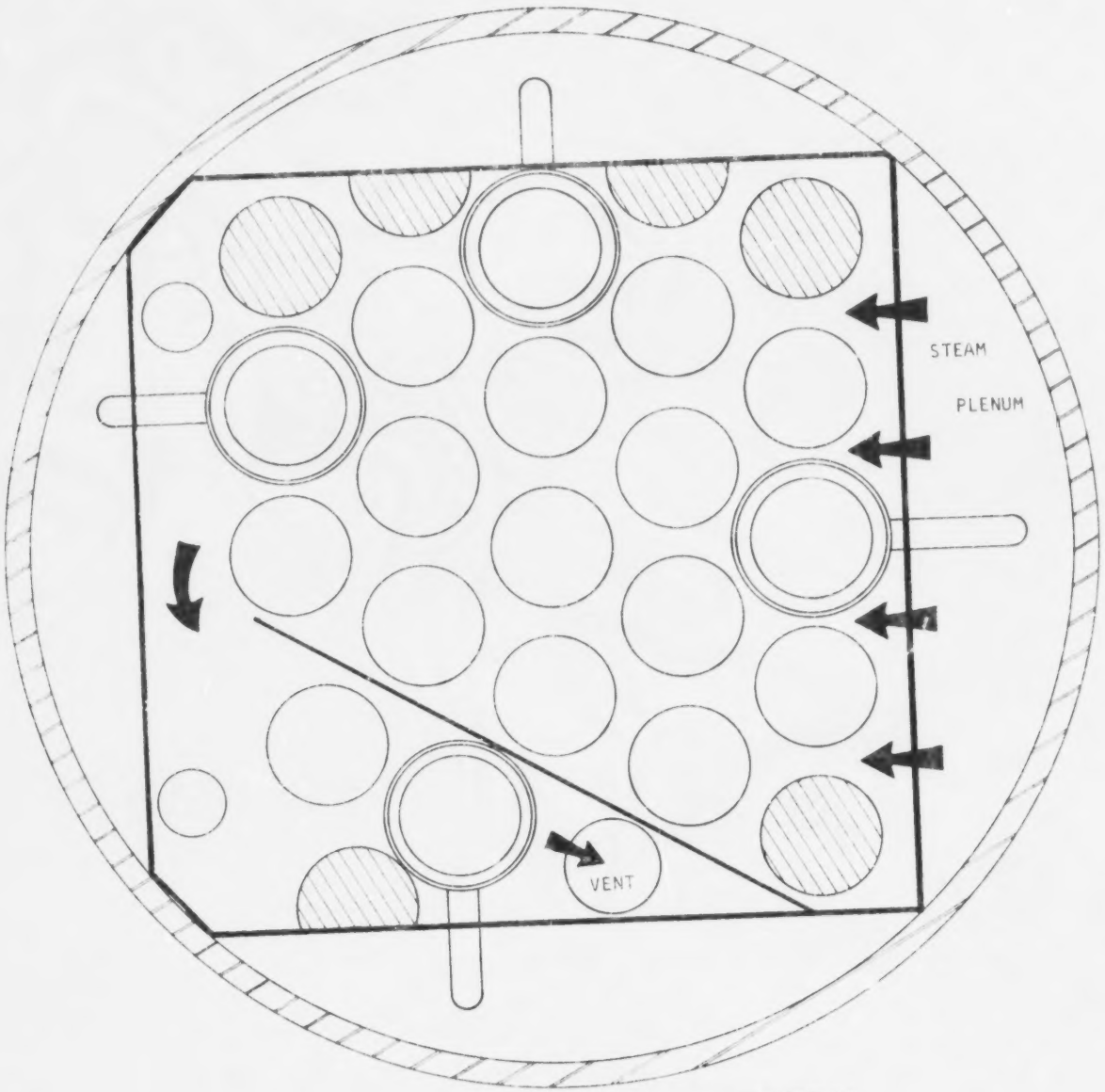
UPFLOW VERTICAL TUBE EVAPORATION PILOT PLANT FIGURE 2

18-tube bundle the condensates off the steam-sides of these tubes were collected and their rates of flow measured, individually for 4 selected tubes and, collectively for the remaining 15 tubes. These measurements showed that variations in flux for individual tubes were within 2 percent. A measured fraction of the total steam flow was vented from the 18-tube bundle and condensed, to remove noncondensables and to assure positive flow across the steam-sides of the tube bundle. All these steam-side condensates were maintained under vacuum and returned to the reboiler loop with which it comprised a closed cycle.

Having the steam-side temperature (Ts) controlled at a level present on the automatic controller, the desired temperature difference (ΔT) across the walls of the 18-tube bundle depended upon the total heat flux (Q) and the duty of the heat reject loop shown on the left of Figure 1. In order to maintain this duty at a steady rate, a large volume of relatively hot water coolant was recirculated under moderate pressure (40 psig) through the heat reject loop at about 1,000 gallons per minute, and cold water was constantly injected into this coolant with the simultaneous rejection of hot water from it. The ΔT for the VTE loop was in this way controlled at any desired level ($\pm 0.1^{\circ}F$), after the steam-side temperature, Ts, became stabilized at its selected, preset level ($\pm 0.1^{\circ}F$).

Wastewater feed was admitted into the VTE loop under vacuum, and recirculated at about $100^{\circ}F$ until deaeration was completed under evacuation. The steam-sides of the tubes were in a dark-brown, oxidized-annealed and fully stabilized condition after intermittent operation for about 2 years without any reconditioning. The 18-tube bundle and steam-side flow pattern are shown in Figure 3, providing positive flow across the entire bundle and a measured vent rate (3-10%) collected along the entire length of the tube bundle.



STEAM SIDE FLOW PATTERN

Distillation tubes were spaced 0.5-inch on a triangular pattern, with dummy tubes (shaded) and baffles to ensure continuous steamside flow from the plenum to the vent tube along the entire bundle length. The vent tube had 0.125-inch holes drilled at 6-inch intervals along its entire length for adequate vent collection.

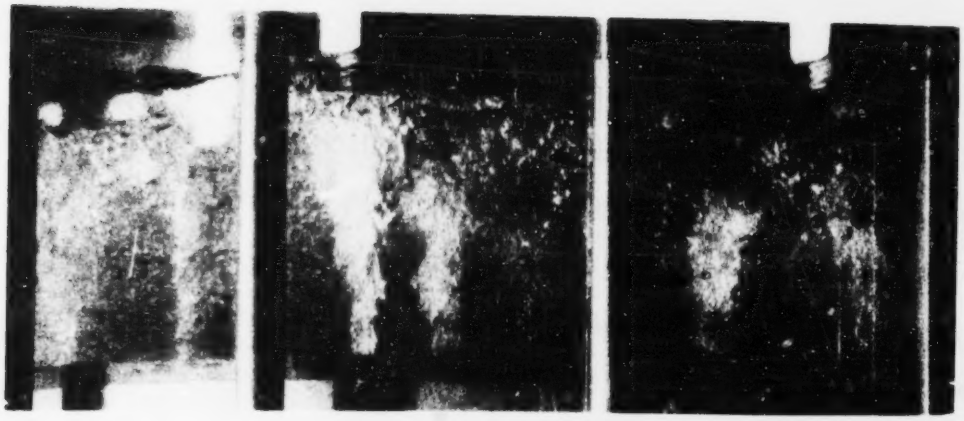
FIGURE 3

Under typical operating conditions, the temperature of the deaerated feed was adjusted to correspond with the steam-side temperature ($\pm 1^{\circ}F$) by passing it through a steam-heated exchanger, controlled by an automatic steam control valve, and was then dumped into a standing leg. From this standing leg the feed flowed through the feed distributor into the inlet ends of the 18-tube bundle, under force of gravity and in response to the inter-effect temperature difference. Upon passing through the orifice plate, the feed flashed down to provide a two-phase vapor-brine system for evaporative flow up the tubes. Two-phase flow up the tubes was maintained by the vapor released from the brine; continuous evaporation of the brine was supported by heat passing through the tube wall from the steam condensing on the steam-sides of the tubes. The hydrodynamic pressure drop through the tubes, measured in a direct manner by means of sight glasses communicating with the tube inlet ends (post-orifice) and with the vapor release vessel, provided a continuous indication of the hydrodynamic oscillations and of the upflow stability in the distillation tubes. The pressure drop across the orifice plate, and the hydrostatic pressure of the feed before passing through the orifice plate, were also measured with manometers. Outflow of brine from the tubes was usually in the form of an annular layer on the tube inner wall, while the vapor phase flowing up in the center of the tube was relatively free of liquid. A discontinuous, gushing mode of outflow was usually observed, with the annular brine layer emerging in spurts, but with the vapor core flow appearing to be continuous. Entrainment separation from the vapor produced was readily accomplished with an impingement plate and a mesh demister positioned about 20 inches above the tube outlet ends, in the vapor release vessel shown in the top center of Figure 1. Primary separation at the tube outlet ends was aided by having the tubes extended above the upper tube sheet, and by having slots

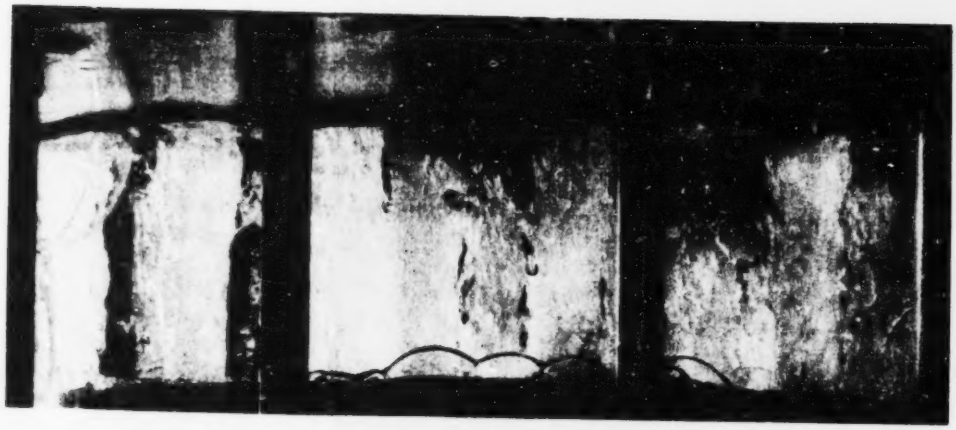
or holes in this part of the tube. The vapor produced was condensed in the heat reject loop and returned to the brine loop.

Temperature measurements were made with platinum-resistance probes providing a direct, digital display of steam-side temperature (Ts), of feed temperature below the orifice plate (Tf), of final brine temperature (Tb) immediately after passing through the vapor release vessel, and of the temperature difference ($\Delta T = Ts - Tb$). These data were checked by measuring the vapor pressures on the steam-side (Ps) and the brine-side (Pv) with an absolute manometer and correcting for boiling point elevation, and by mercury-filled thermometers installed in direct contact with the flowing fluids.

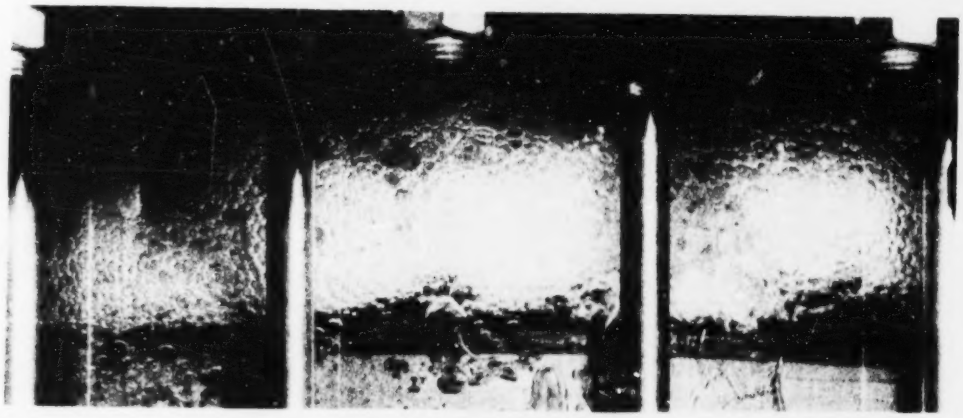
Upflow VTE heat transfer data were obtained under steady-state operating conditions, first without any addition of surfactant to wastewater feed, and then with specific concentrations of a selected surfactant added to this feed. Data without surfactant additives compared well with those obtained earlier in an OSW sponsored test series with this pilot plant. The interface-enhanced data were obtained with the same process conditions, after the addition of a selected surfactant (Neodol-25-3A, or Neodol 25-3S, Shell Chemical Company) to the wastewater feed. Surfactant addition was observed to bring about a significant change in the mode of two-phase flow, characterized by foaming at the inlet and outlet ends of the tubes and by a substantial reduction in the tube pressure drop, ΔP. These typical modes of flow through the orifice plate, spaced about three inches from the tube inlet ends, are shown in Figure 4. Without a foaming agent additive the feed flashed down at the orifices into a continuous liquid layer, with the vapor and feed liquid passing through this liquid layer into the tube inlet ends. After the addition of surfactant the feed flow was radically changed. Flashdown at the orifice plate produced foamy jets passing through a vapor-filled space into the tubes. This mode



a. Without Foaming Agent Added to Feed.



b. With Foaming Ager Added, and Orifices in Line with Tube Ends.



c. With Foaming Agent, and Orifices Offset from Tube Ends.

TYPICAL TWO-PHASE FLOW THROUGH VTE ORIFICE PLATE

FIGURE 4

of flow is associated with a substantial reduction in the hydrodynamic pressure drop (ΔP) through the distillation tubes, by a factor of 3 to 10 compared to the typical ΔP without surfactant additives. Rotating the orifice plate to cause impingement of some of the foamy jets against the tube sheet filled this entire space with foam and produced a further increase in performance. This is of significance because one can thereby ensure wetting of the tube inlet section with foam by means of secondary orifices placed interstitially of the regular orifices that are lined up with the tubes.

The mode of foamy two-phase flow from the tube outlet ends after the addition of surfactant, is shown in Figure 5. The residual liquid, carried through the tubes by the vapor phase core flow, is ejected as a foamy annulus in contact with the tube inner wall; this liquid or foam phase flow is discontinuous or gushing randomly from the 18 tubes.

UPFLOW VTE PYREX GLASS EVAPORATOR

An all-glass Pyrex-tubed evaporator, shown in Figure 6, was constructed with the objective of obtaining data and information on the solute-crystallization behavior of wastewaters. This equipment comprised a pair of Pyrex tube upflow VTE tubes of 1-inch x 5-foot dimensions having steam jackets, and being tangentially connected to a 5-liter spherical cyclone vapor-liquid separator. The top of the cyclone separator was connected via a 2-inch vapor discharge to an efficient vacuum-operated condenser connected to a distillate reservoir which permitted periodic removal of the distillate without interrupting the vacuum-evaporation process. The base of the cyclone separator vessel was connected to a 2-inch diameter standpipe for recirculation. The distilland was recycled back to the distillation tubes via 1/8-inch orifices provided in the form of Pyrex glass valves fused to the inlet ends of these tubes.

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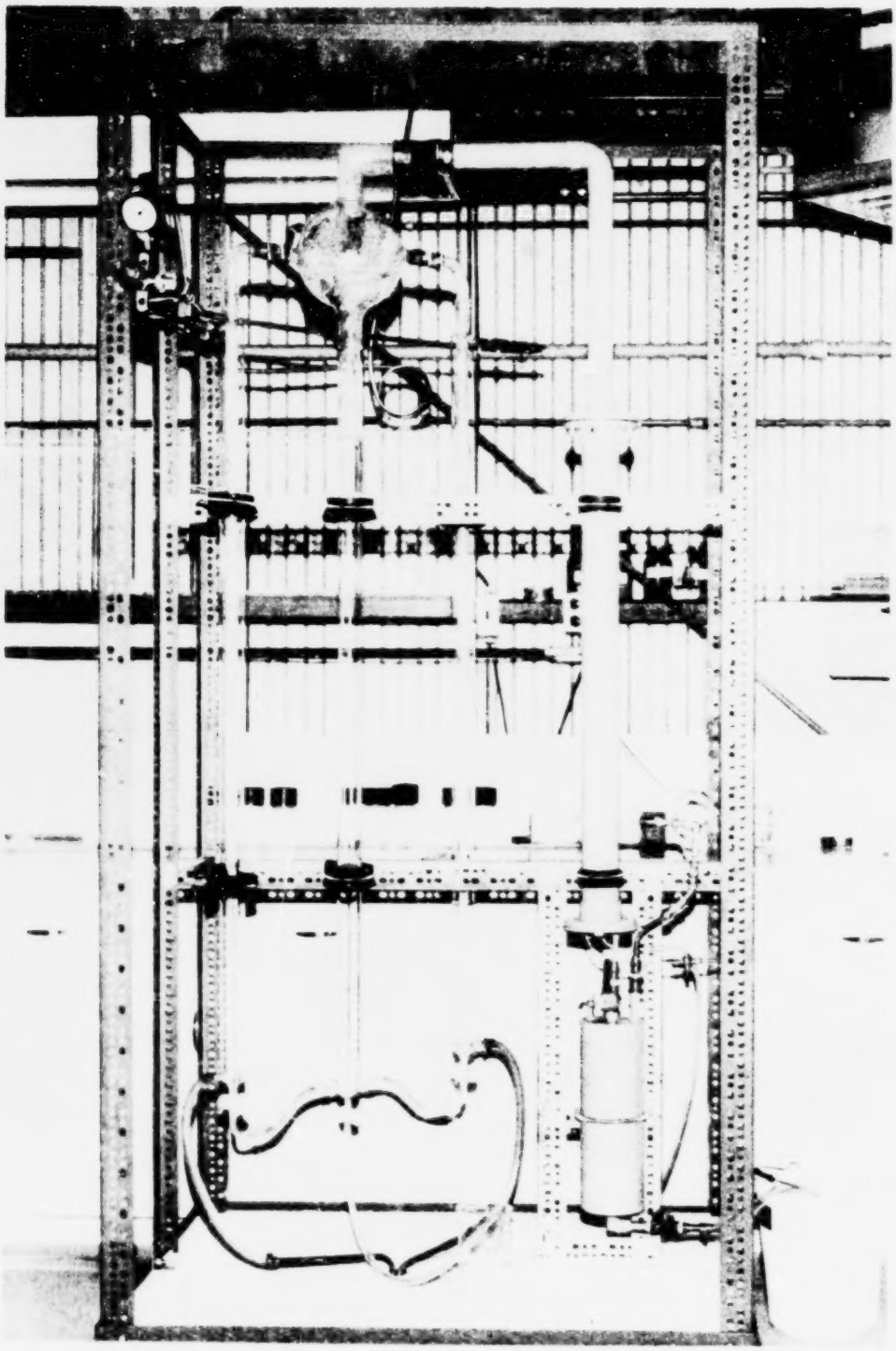
FOAMY ANNULAR FLOW FROM DISTILLATION TUBES

FIGURE 5



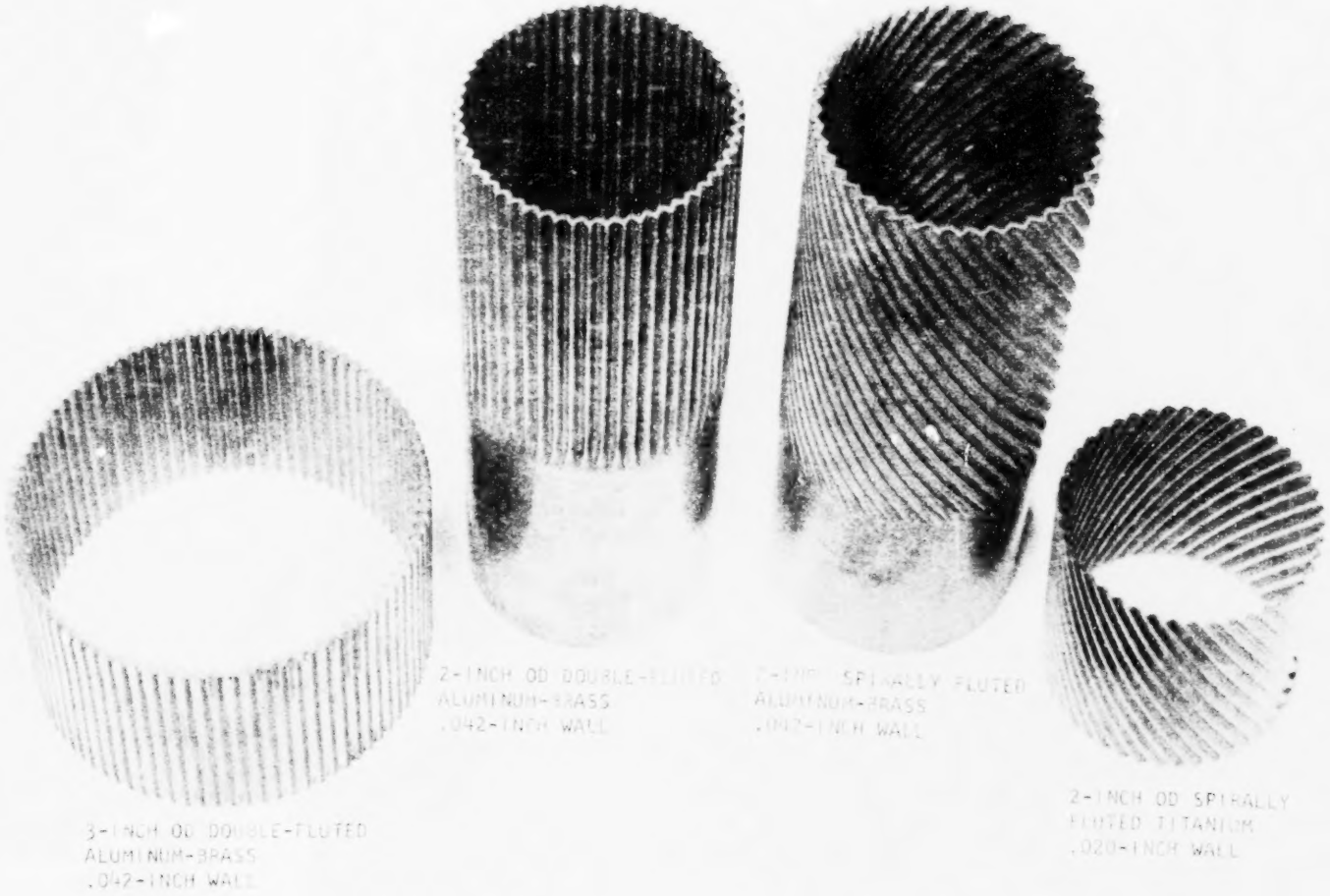
PYREX TUBE CRYSTALLIZING EVAPORATOR FIGURE 6

The minimal liquid holdup in this apparatus was bout 800 ml, and its capacity was about 4 liters when full. Provision was made for the continuous addition of feed during evaporation, thus providing concentration of waste-water feed by any desired factor. This permitted close observation of the modes of two-phase flow with and without the addition of a surfactant to the feed, and of the concentration levels at which percipitates were formed.

Operation of this evaporator under vacuum conditions was provided by a rotary oil vacuum pump protected by a final condenser. Typical evaporation temperatures were in the range of 90 to 110°F depending upon the solute content of the distilland, and the cooling water temperature. The ΔT applied was such as to provide a heat flux through the walls of the distillation tubes about equal to that of aluminum-brass tubes of the same dimensions used at a conventional ΔT of about 10°F.

DISTILLATION TUBES USED IN THE VTE PILOT PLANT

The VTE heat transfer tubes used in this study were all of the double-fluted or enhanced type, having their walls formed into axial or spiralled grooves or flutes. This provides complementary flutes on both the inside and outside (brineside and steamside) surfaces of the tubes. This type of wall modification provides an approximately 5-fold increase in the steamside coefficient at an additional cost of about 30 percent added to the cost of the smooth tube from which the double-fluted tube is formed (9). Such tube profiles are shown in Figure 7.



AXIALLY AND SPIRALLY DOUBLE-FLUTED DISTILLATION TUBES

FIGURE 7

EXPERIMENTAL WORK

1) Investigation of Cooling Tower Blowdown

Background. The adoption of evaporative cooling for steam power plants to reduce their environmental impact by limiting undesirable effluents projects the need for an economically acceptable method of renovating cooling tower blowdown. Vertical tube evaporation to further concentrate the blowdown to the concentration limits permitted by its solute content, followed by crystallizing-evaporation to a slurried salt residue, relies on well-defined and acceptable technology (12). If these evaporation procedures are performed at relatively low temperatures, one can utilize heat rejected from the power plant as the driving force for evaporation; low temperature evaporation increases the acceptable concentration limits of calcium and magnesium salts in the blowdown brine and reduces corrosion and fouling problems of equipment. While heat of evaporation is essentially free at these low temperatures (around 120°F) the evaporator performance is rather low, requiring a relatively large heat transfer surface area and increased capital costs. Methods of increasing the evaporator heat transfer performance, thereby reducing the capital cost, provides an even more substantial overall cost reduction on this low temperature evaporation than in the case where the cost of fuel has to be included. Interface enhancement (1, 2, 3, 4) offers a novel and promising method of increasing the performance of vertical tube evaporation (VTE) at quite low added cost, while it concurrently reduces the potential for scaling, fouling and corrosion of the evaporator.

VTE performance data. A large batch of cooling tower blowdown (1,500 gallons) was collected from the Mohave Power Plant with the assistance of the Bechtel Power Corporation in November 1973, and trucked to the VTE pilot plant facility for these tests. It had a pH of 8.4 and contained close to 10,000

ppm of total dissolved solids. This blowdown was slightly turbid, and was used as such without clarification.

The heat transfer enhancement effect and the tubeside pressure drop reduction effect responsive to the gradual addition of a surfactant to the blowdown brine during upflow VTE under typical steady state process conditions are shown in Figure 8. The evaporator performance (U) at 210°F was approximately doubled by the addition of 5 ppm of Neodol-25-3A (Shell Chemical Company) while the pressure drop (ΔP) was simultaneously reduced from about 30 to 7.5 inches of water. Further additions of surfactant up to 25 ppm produced a gradual further heat transfer enhancement to 3,000 Btu per hr-ft^2-°F. The most effective surfactant concentration was about 10 ppm, which provided a 120 percent enhancement of the overall heat transfer coefficient. The tubeside pressure drop was also at a minimal value of 5-inches of water with 10 ppm of additive.

The overall heat transfer performance through the available evaporation temperature range of 120 to 220°F under typical multi-effect upflow VTE conditions, obtained without, and with 10 ppm of Neodol additive to the blowdown brine feed are shown in Figure 9. It is apparent that, in the case without surfactant addition, the performance was maximal at 180°F; this indicates that some fouling or scaling occurred at the higher brine temperatures even with the pH of the brine adjusted to 6.8. On the other hand, a substantial increase in performance was obtained at these process conditions after the addition of 10 ppm of a surfactant. Interface enhancement was somewhat less effective in the 120 to 140°F range at this low a surfactant concentration. This should be improved by using a somewhat higher surfactant concentration and by using 3-inch diameter tubes (5).

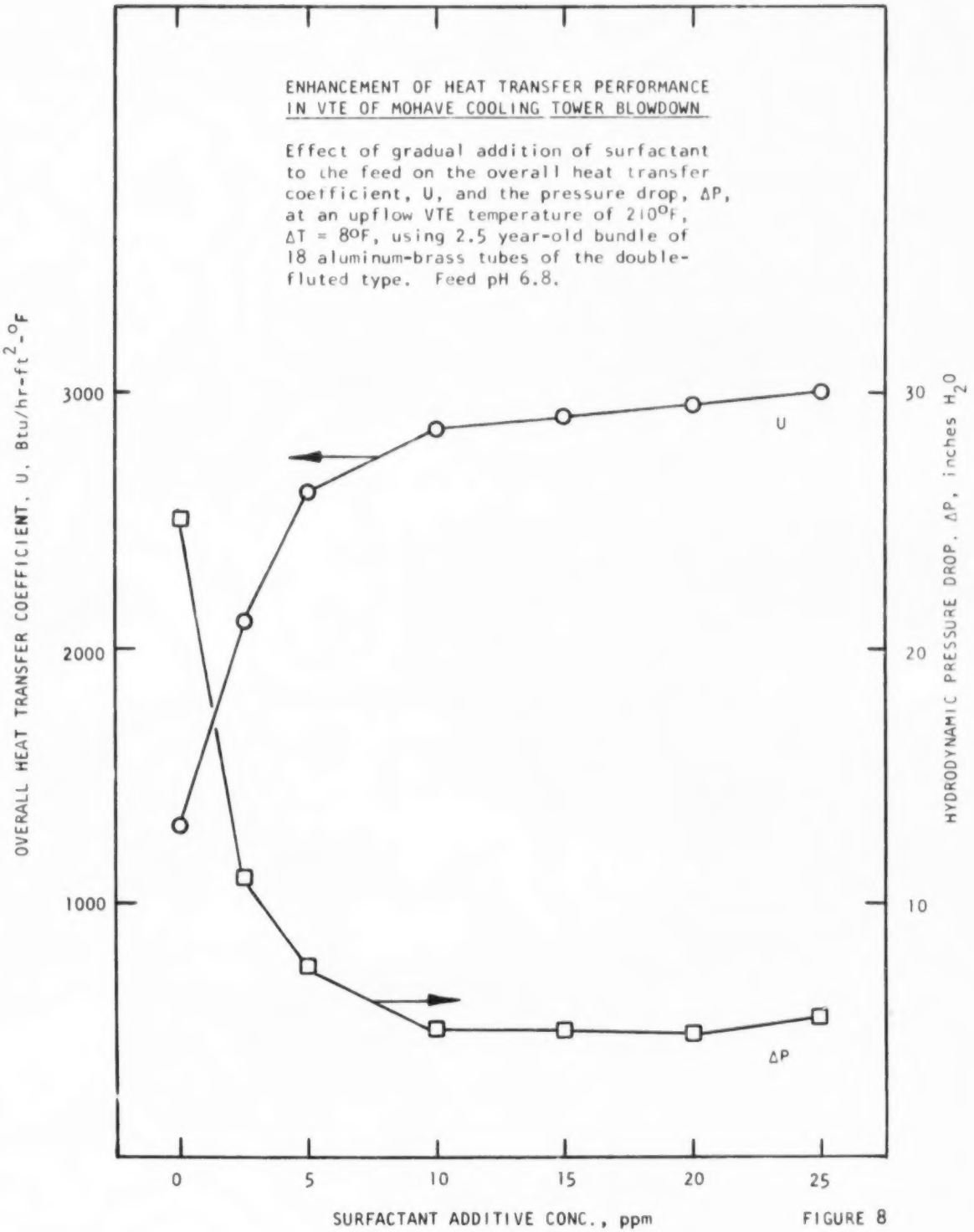

ENHANCEMENT OF HEAT TRANSFER PERFORMANCE
IN VTE OF MOHAVE COOLING TOWER BLOWDOWN
Effect of gradual addition of surfactant to the feed on the overall heat transfer coefficient, U, and the pressure drop, ΔP, at an upflow VTE temperature of 210°F, ΔT = 8°F, using 2.5 year-old bundle of 18 aluminum-brass tubes of the double-fluted type. Feed pH 6.8.
OVERALL HEAT TRANSFER COEFFICIENT, U, Btu/hr-ft²-°F
HYDRODYNAMIC PRESSURE DROP, ΔP, inches H2O
3000
2000
1000
30
20
10
U
ΔP
0
5
10
15
20
25
SURFACTANT ADDITIVE CONC., ppm

FIGURE 8

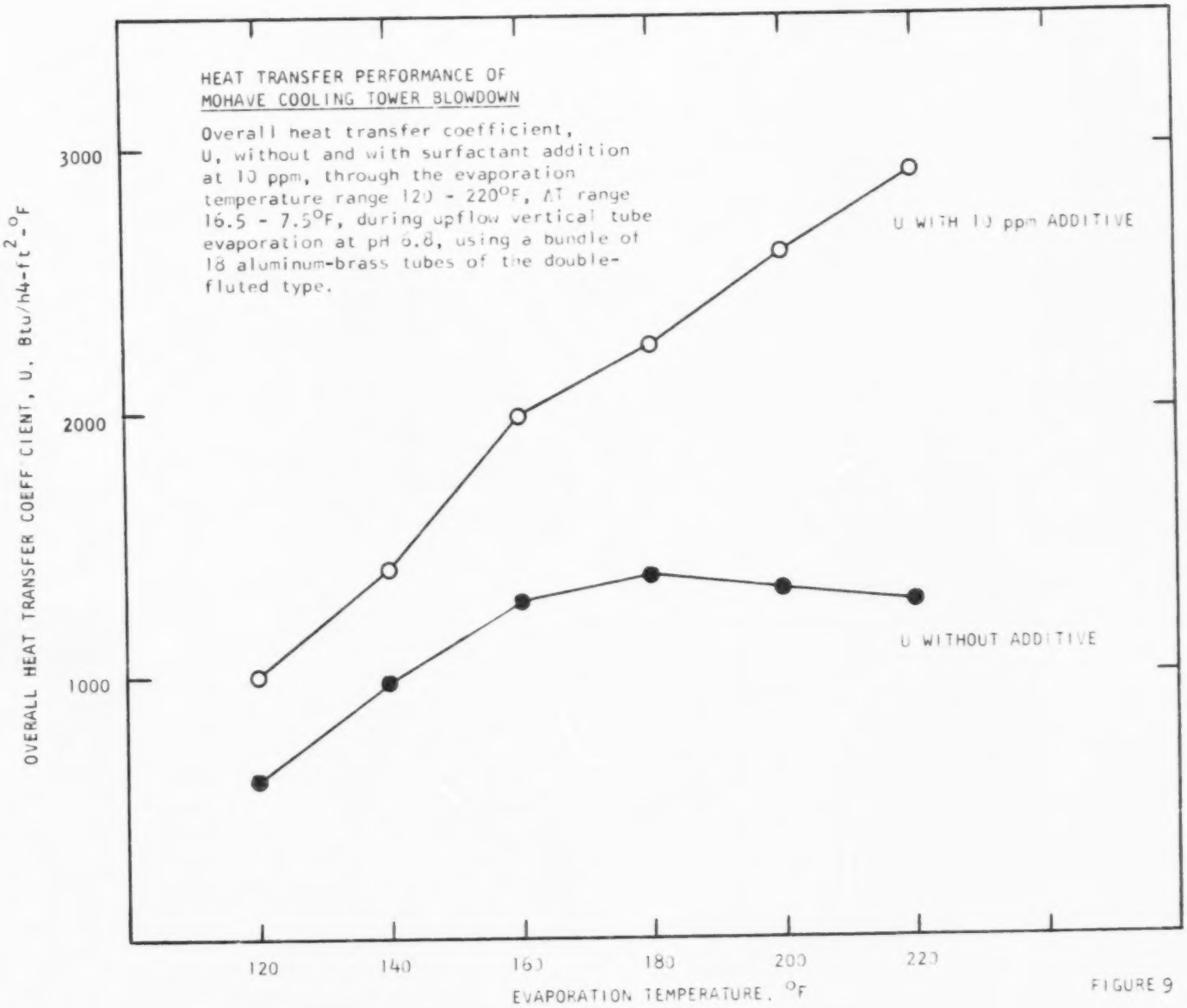

HEAT TRANSFER PERFORMANCE OF
MOHAVE COOLING TOWER BLOWDOWN
Overall heat transfer coefficient, U, without and with surfactant addition at 10 ppm, through the evaporation temperature range 120 - 220°F, ΔT range 16.5 - 7.5°F, during upflow vertical tube evaporation at pH 8.8, using a bundle of 18 aluminum-brass tubes of the double-fluted type.
U WITH 10 ppm ADDITIVE
U WITHOUT ADDITIVE
OVERALL HEAT TRANSFER COEFFICIENT, U, Btu/h4-ft²-°F
3000
2000
1000
120
140
160
180
200
220
EVAPORATION TEMPERATURE, °F

FIGURE 9

Figure 10 shows the upflow VTE performance (U) during the concentration of cooling tower blowdown by interface-enhanced evaporation at 130°F, in comparison with conventional evaporation (broken line). Also shown are performance data calculated after deducting the ΔT loss due to apparent boiling point rise as observed. The steamside temperature was held at 142°F and the condenser flux was held at steady state for these data. Some precipitate formation was observed at brine concentrations of 2 percent and higher. A slight increase in performance was observed as the brine concentration increased from 1 to 1.67 percent, in spite of the increased solute content of the brine. This is attributable to the simultaneous concentration of the surfactant in the brine, which increases the evaporation coefficient as indicated by Figure 8, and as also reported in earlier work (8). The decline in performance at brine concentrations beyond the onset of crystallization is attributable to the loss of surfactant from solution due to its adsorption on the crystal or precipitate surfaces. This rationale requires confirmation in further work planned.

A relatively inexpensive and effective method of stripping surfactant additives from blowdown brines, by foam fractionation, has been developed in this Laboratory, and demonstrated on a pilot plant scale (13). This procedure also clarifies the brine concentrate and facilitates its further concentration in a crystallizing evaporator to produce useful salts, such as sodium sulfate, and a final slurried concentrate for ponding or disposal. The foamate fraction containing the surfactant concentrate can be recycled after its clarification.

Discussion. The use of surfactant additives in blowdown concentration by VTE utilizing waste heat available in a power plant cooling cycle provides significant improvements in process flexibility and economy (11). Figure 11 shows a possible method of integrating this coolant renovation-recycle system into

CONCENTRATION OF MOHAVE POWER PLANT COOLANT BLOWDOWN
BY INTERFACE-ENHANCED VERTICAL TUBE EVAPORATION AT 130°F

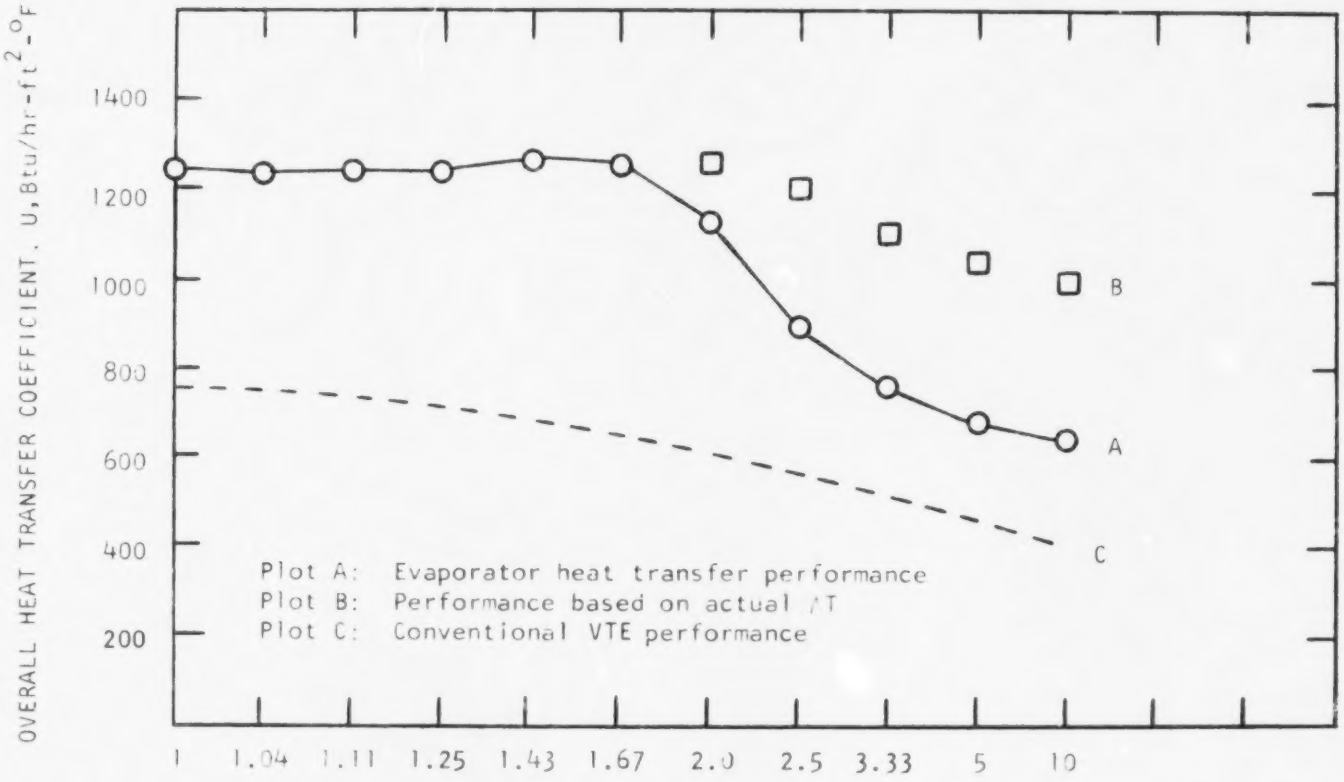
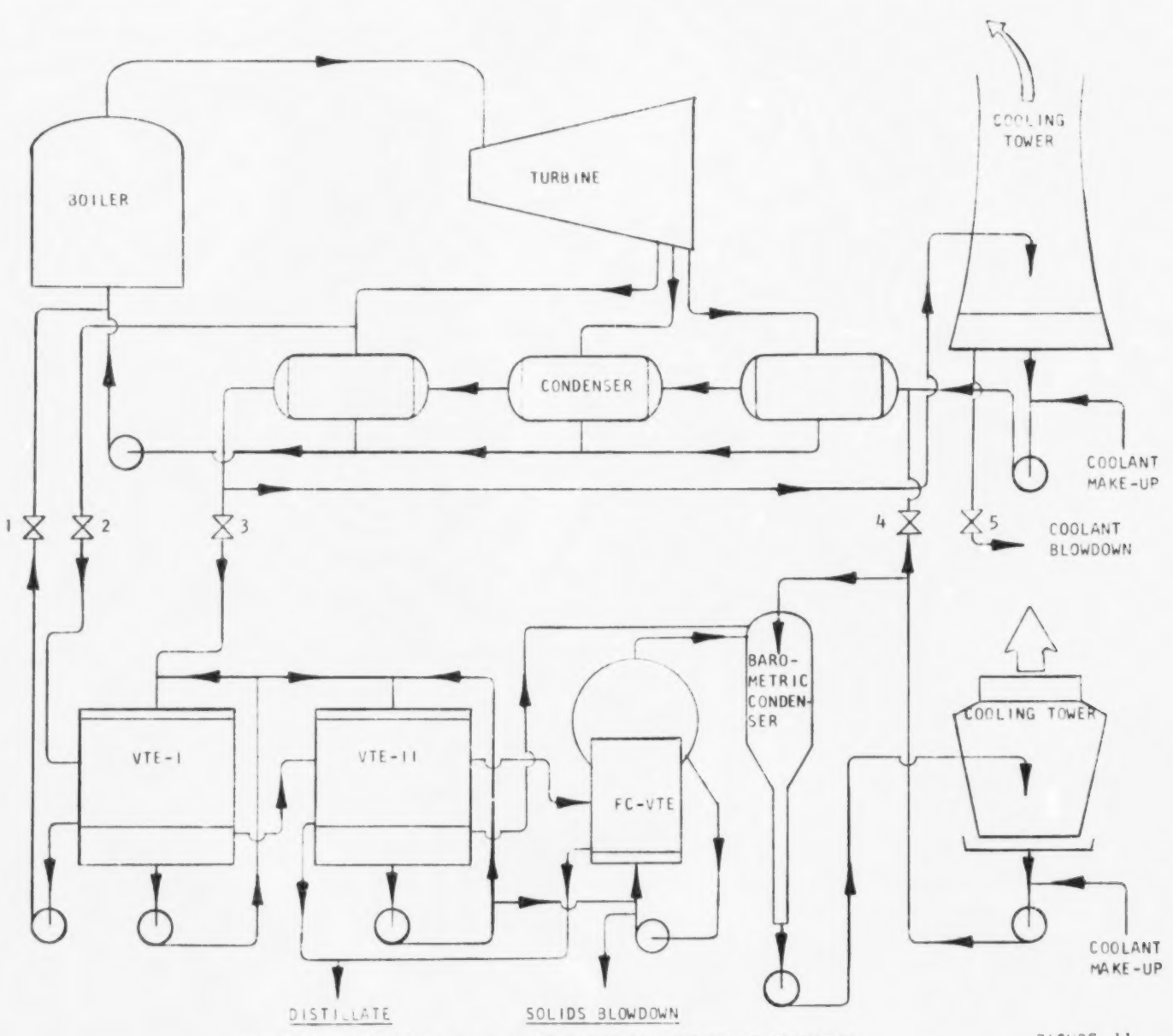


FIGURE 10



RENOVATION AND RECYCLE OF POWER PLANT COOLING TOWER BLOWDOWN

FIGURE 11

the flow diagram of an existing power plant. The upper half of Figure 11 represents an existing power plant coolant cycle; the lower half shows the renovation loop added on via 4 valves, permitting shutdown of this loop and reversion to the original cycle of operation, if desired. The power plant could be reverted to the original mode of operation at any time within the time required to close valves 1, 2, 3 and 4, and opening valve 5 to resume the usual discharge of blowdown, for instance to a reservoir for later renovation. Since about 5 percent of the total turbine exhaust steam is utilized in the evaporator loop (via valve 2) a small forced-draft cooling tower is added to this loop to make up for the reduced demand on the power plant cooling tower. The condensate of this exhaust turbine steam is returned from the first effect (VTE-I) to the boiler via valve 1. A portion of the hot coolant is diverted to the evaporation loop, as blowdown, via valve 3. The vapor produced in VTE-I serves as heating steam for the VTE-II and the forced circulation crystallizing evaporator (FC-VTE), and these condensates are available (DISTILLATE) for a beneficial use such as boiler feed makeup or potable fresh water or for return to the main coolant loop. Vapors produced in the VTE-II and FC-VTE are returned to the main coolant loop as condensates from the barometric condenser via valve 4; dilution of the coolant with condensates reduces coolant makeup and pretreatment requirements. The coolant makeup for the barometric condenser and small cooling tower need not be softened since it is continuously diluted with this distilled water, and becomes part of the main coolant loop. Another option is to divert the DISTILLATE (from VTE-II and FC-VTE) to serve as coolant makeup for the small cooling tower, in which event this coolant will be distilled water entirely; this provides a source of cooled distilled water (as blowdown) for the above beneficial uses. It is apparent that the rate of producing such cooled

distillate will depend on the rate of turbine exhaust steam flow through valve 2, and it can be substantially increased by partial replacement of main cycle condenser capacity with additional heat duty in the VTE's, barometric condenser and small cooling tower.

In addition, the further adoption of this proposed means of evaporative cooling, to partially replace cooling condensers in future power plants, can provide the significant beneficial result of producing more distilled water than that required to maintain scale-free operation of a cooling tower. This additional, pure distilled water product could in part be diverted for another beneficial use, for instance, for boiler feed makeup and to reduce the salinity of a domestic or municipal water supply. In relation to the proposed Palo Verde power plant, where secondary or tertiary treated municipal effluents are to be used for power plant cooling, the adoption of this proposed coolant recycle scheme could provide some pure, distilled water, for instance for the dilution of Colorado River water to reduce its salinity. This technology will also provide increased flexibility in coolant pretreatment; for instance, the need for softening may be reduced, thereby reducing chemical costs as well as final saline wastes. Since the coolant is stripped of volatile constituents by repeated passage through the cooling towers, the subsequent evaporation of the blowdown should produce pure distilled water of potable quality.

Conclusions. It is clear from the above data and observations that the interface-enhanced mode of VTE operation can provide a substantial increase in the heat transfer performance during blowdown evaporation, especially at blowdown concentrations below the crystallization or precipitation limit. This limiting concentration is increased by the presence of the surfactant additive, probably by interfering with the rate of crystal growth through adsorption of the additive on newly formed crystal surfaces.

The benefits of increased heat transfer performance are mainly as follows:

(a) It permits the use of an increased number of effects in the multi-effect VTE plant while maintaining the per-effect distillate production at a lower per-effect ΔT than in conventional VTE operation (4). This permits a proportionate increase in the gain ratio, in the interest of substantial steam or fuel savings. This aspect of interface enhancement also improves design flexibility, permitting an improved design optimization with reference to capital versus operating costs.

(b) Blowdown brine concentration with waste heat accentuates the significance of interface enhancement for reducing capital costs. This applies to both upflow and downflow VTE operation. It also permits the production of distilled water by allowing the inclusion of a two-effect downflow VTE within the waste heat temperature span available in a power plant cooling cycle, as shown in Figure 11.

(c) Interface enhancement can be applied to vapor compression VTE operation for cooling tower blowdown renovation to reduce the required heat transfer surface in such an installation.

(d) Operation and maintenance costs of blowdown evaporators should be reduced by the use of surfactant additives because of the particulate dispersant effects of surfactant; this should reduce fouling and corrosion of heat transfer surfaces.

Solute precipitation data. Observations made in earlier work, and data obtained with the Pyrex tube evaporator indicated that the dispersant effect of the surfactant additive delays the onset of crystallization. This side effect is quite beneficial; it can reduce the capacity requirements of the relatively expensive crystallizing evaporator to be used subsequently.

In a typical run, 16 liters of Mohave blowdown was evaporated at 130°F to a residual volume of 1.8 liters (in 1.5 hours), at which concentration a crystalline precipitate was first observed. This concentrated residue was withdrawn and separated into a 50 ml fraction containing a muddy sediment and a clear supernatant fraction (1.75 liters) from which further crystallization occurred over the next 48 hours. In a follow-on run with surfactant addition at 8 ppm to the feed, 20 liters of Mohave blowdown having 0.3 ml of Neodol-25-3-S (Shell Chemical Co.) added was similarly evaporated at 130°F to a residual volume of 1.66 liters (12-fold concentration) when a crystalline precipitate was first observed. This residual concentrate was separated into a 25 ml fraction containing a muddy precipitate and a clear fraction (1.63 liters) from which further crystallization occurred over the next two days. It was apparent from these tests that the addition of a surfactant depresses the crystallization of solutes during evaporation of Mohave coolant blowdown.

2) Industrial Steam Generator Blowdown Concentration

Large industrial boilers produce a considerable volume of concentrated blowdown, depending upon the quality of the feed water used. The blowdown from steam generators serving a large refinery can reach 500,000 gallons per day on the basis of using treated tapwater as boiler feed. The proportion of blowdown to feed is determined by the scaling potential of the pre-treated feed and the need to keep boiler heat transfer surfaces free of corrosion, fouling and scaling in the interest of high heat transfer performance and fuel economy. The concentration in the blowdown of the naturally occurring salts, as well as of boiler feed additives such as antiscaling compounds and corrosion inhibitors could render it unsuitable for discharge to, for instance, a municipal effluent treatment plant.

It was the objective of this series of tests to determine the feasibility of using the interface-enhanced method of VTE operation to reduce industrial boiler blowdown to a very small volume while simultaneously producing distilled water of pure quality suitable for a beneficial use.

The use of surfactant additives as evaporator heat transfer performance enhancement agents had been demonstrated and was anticipated to also be effective for boiler blowdown. A second beneficial effect of these additives previously observed is to inhibit the formation of scale and to act as a dispersant for particulate matter in suspension.

Three series of tests were carried out with the blowdown obtained from a large industrial steam generation plant. These test series were;

(a) Typical upflow VTE heat transfer performance data using the 5,000 gpd pilot plant tubed with 2-inch OD x 10-foot long double-fluted aluminum-brass tubes.

(b) Test data on the upflow VTE heat transfer enhancement response and the pressure drop reduction effect responsive to the gradual addition of a selected surfactant to boiler blowdown fed evaporated at 210°F.

(c) Interface-enhanced upflow VTE performance data through the range of typical effect-to-effect process conditions, comparable to the data shown under (a).

(d) Heat transfer performance and solute precipitation behavior during the gradual 10-fold concentration of boiler blowdown having 10 ppm of a selected surfactant added.

(e) Solute precipitation behavior during the gradual 20-fold concentration of boiler blowdown having 10 ppm surfactant added, examined during evaporation in the Pyrex glass upflow VTE.

(a) Typical upflow VTE data: Figure 12 shows the overall heat transfer coefficient and tubeside pressure drop data obtained with boiler blowdown (adjusted to pH 6 by the addition of sulfuric acid) under the usual multi-effect evaporation temperature, temperature difference (ΔT) and feed flow conditions. Data are shown for double-fluted aluminum-brass and copper tubes of 2-inch OD x 10-foot heated length. These data are consistent with earlier tests on freshwater and seawater obtained in this laboratory and elsewhere (3). The heat transfer performance with 2-inch tubes is generally low in the 120 to 160°F range where the tubeside pressure drop is relatively high and the upflow stability low. These tubes perform satisfactorily in the 160 to 240°F range; 3-inch diameter tubes would be preferable for the lower range.

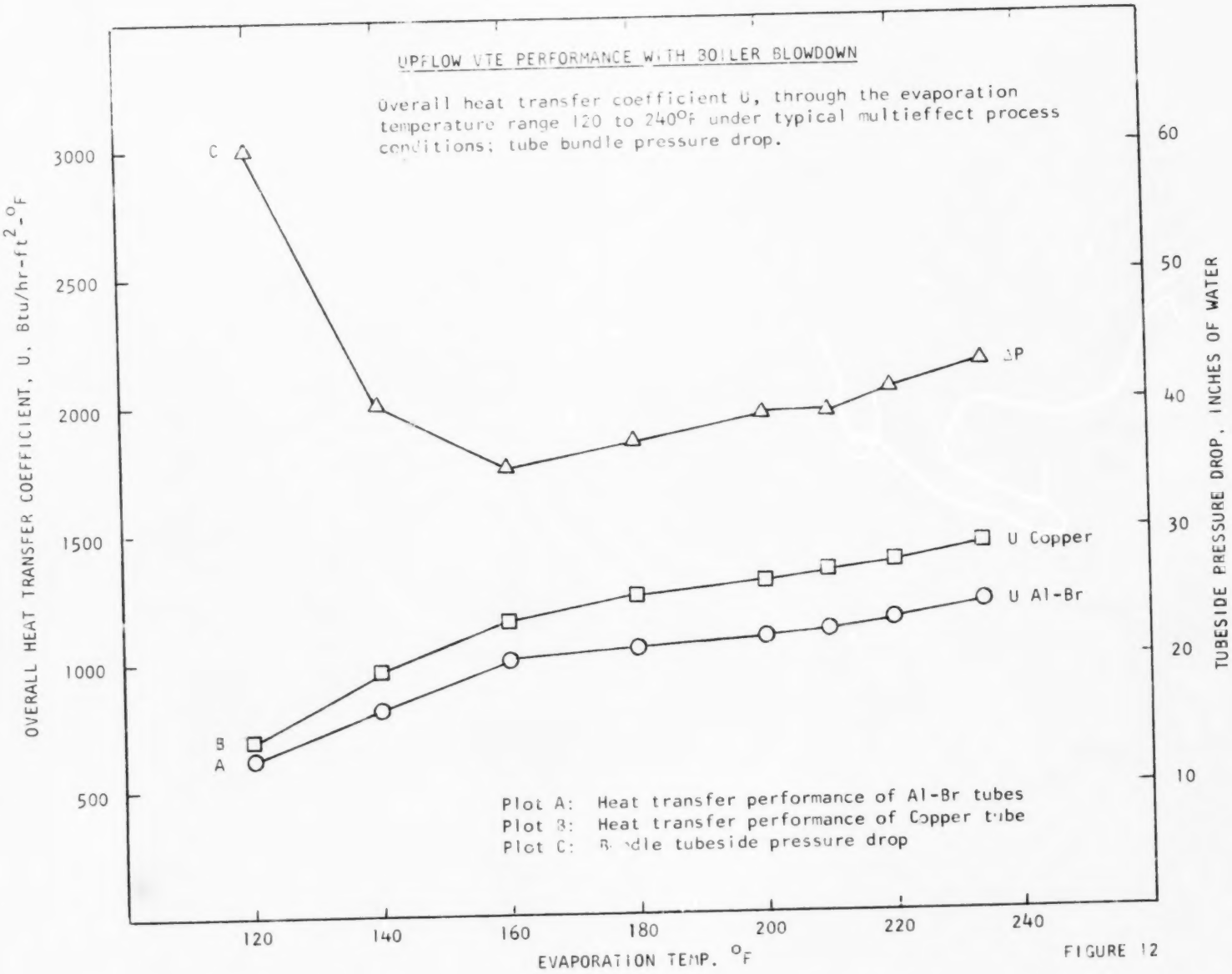

UPFLOW VTE PERFORMANCE WITH BOILER BLOWDOWN
Overall heat transfer coefficient U, through the evaporation temperature range 120 to 240°F under typical multieffect process conditions; tube bundle pressure drop.
OVERALL HEAT TRANSFER COEFFICIENT, U, Btu/hr-ft^2-°F
TUBESIDE PRESSURE DROP, INCHES OF WATER
EVAPORATION TEMP. °F
3000
2500
2000
1500
1000
500
60
50
40
30
20
10
120
140
160
180
200
220
240
C
ΔP
U Copper
U Al-Br
B
A
Plot A: Heat transfer performance of Al-Br tubes
Plot B: Heat transfer performance of Copper tube
Plot C: Bundle tubeside pressure drop

FIGURE 12

(b) The upflow VTE interface enhancement response with boiler blowdown at an evaporation temperature of 210°F responsive to the gradual addition of Neodol 25-3A (Shell Chemical Co.) is shown in Figure 13. Data were plotted for the overall heat transfer coefficient of the 14-tube bundle of double-fluted aluminum-brass tubes and for a double-fluted copper tube, as well as the tube bundle pressure drop. These data were again consistent with earlier reports (2,3,4), confirming the dramatic pressure drop reduction effect and the substantial performance enhancement by the addition of a surfactant and the imposed foamy two-phase flow of the feed over the heat transfer surfaces. For instance, the 14-tube bundle performance was increased by 117 percent after the addition of 10 ppm of surfactant, while the pressure drop was concurrently reduced by a factor of 11 from 40 to 3.5 inches of water. The comparable response of the copper tube was even better at 149 percent enhancement, consistent with earlier data (3). Further additions of surfactant provided further increases in performance and a slight increase in the tubeside pressure drop; the beneficial maximum surfactant concentration was about 30 ppm.

(c) Figure 14 shows the interface-enhanced upflow VTE heat transfer performance through the usual multieffect evaporation temperature range of 120 to 240°F. These data, in comparison with the data discussed under (a) above (Figure 12), indicate the advantage obtainable by the use of surfactant additives in blowdown evaporation. The distillate productivity rate is about doubled while the tubeside pressure drop is substantially reduced to ensure stable operation of the multieffect upflow VTE.

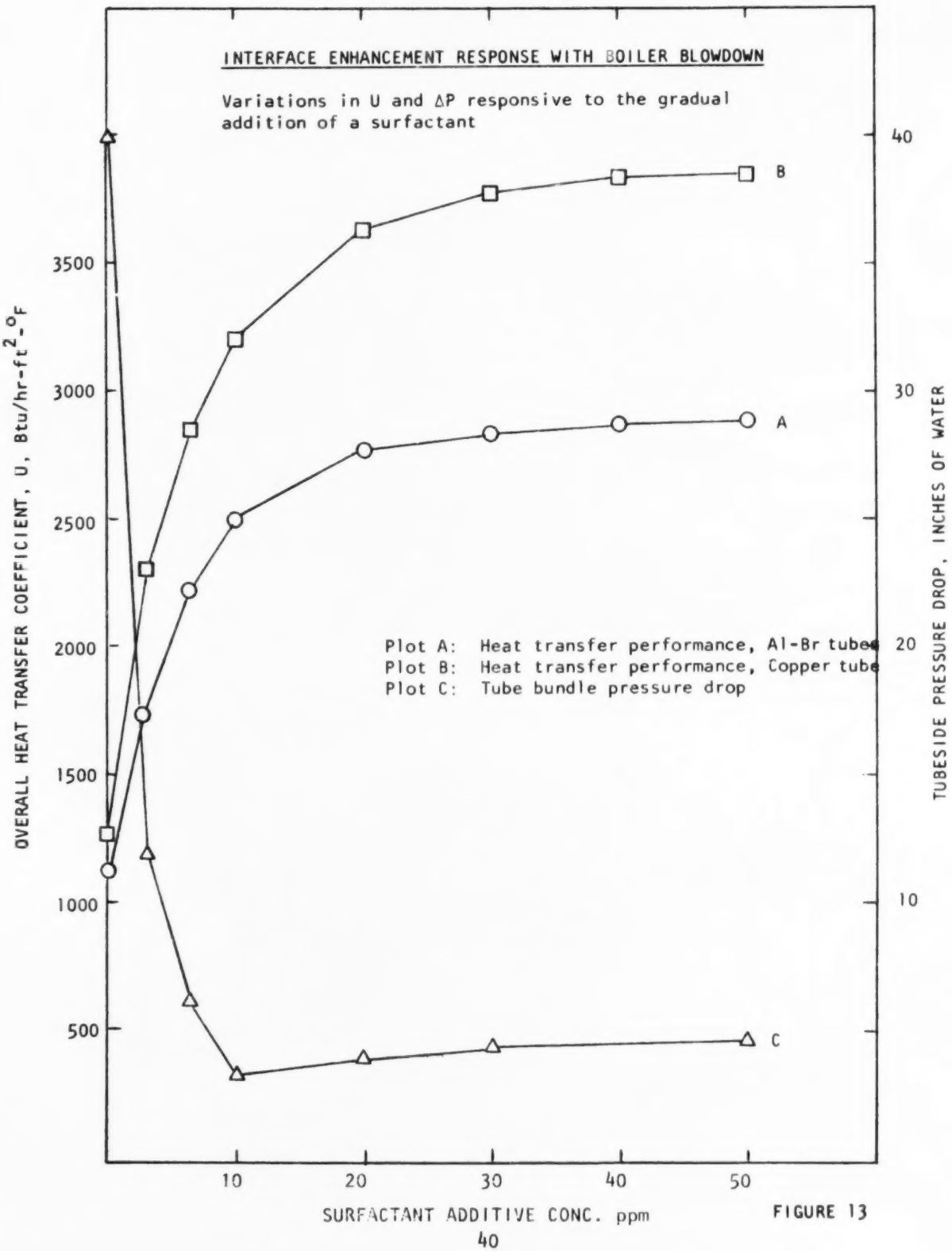

INTERFACE ENHANCEMENT RESPONSE WITH BOILER BLOWDOWN
Variations in U and ΔP responsive to the gradual addition of a surfactant
OVERALL HEAT TRANSFER COEFFICIENT, U, Btu/hr-ft²-°F
TUBESIDE PRESSURE DROP, INCHES OF WATER
SURFACTANT ADDITIVE CONC. ppm
Plot A: Heat transfer performance, Al-Br tubes
Plot B: Heat transfer performance, Copper tube
Plot C: Tube bundle pressure drop
A
B
C
3500
3000
2500
2000
1500
1000
500
40
30
20
10
10
20
30
40
50

FIGURE 13

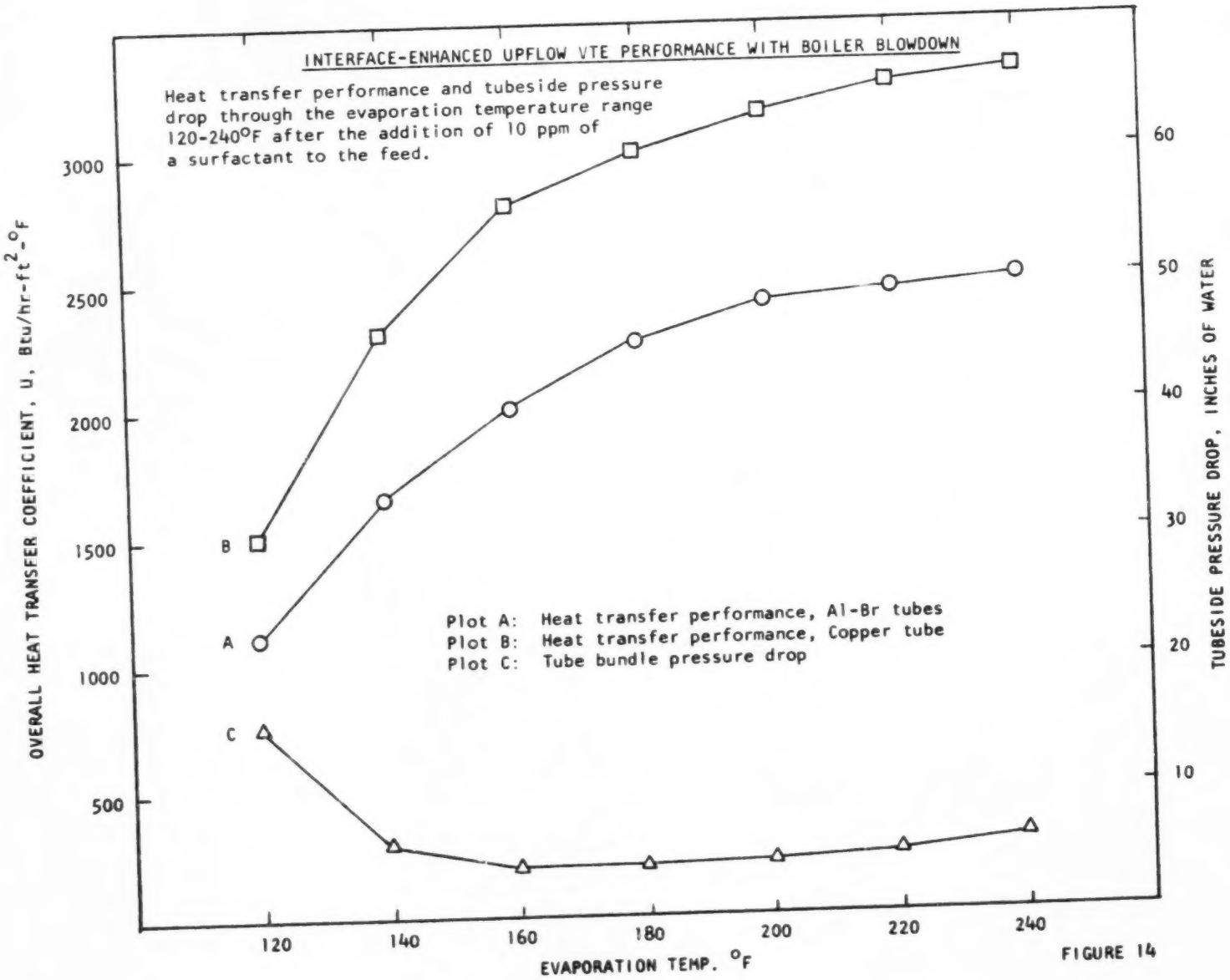

INTERFACE-ENHANCED UPFLOW VTE PERFORMANCE WITH BOILER BLOWDOWN
Heat transfer performance and tubeside pressure drop through the evaporation temperature range 120-240°F after the addition of 10 ppm of a surfactant to the feed.
OVERALL HEAT TRANSFER COEFFICIENT, U, Btu/hr-ft²-°F
TUBESIDE PRESSURE DROP, INCHES OF WATER
EVAPORATION TEMP. °F
3000
2500
2000
1500
1000
500
60
50
40
30
20
10
120
140
160
180
200
220
240
A
B
C
Plot A: Heat transfer performance, Al-Br tubes
Plot B: Heat transfer performance, Copper tube
Plot C: Tube bundle pressure drop

FIGURE 14

(d) A large volume (800 gallons) of industrial boiler blowdown was subjected to a gradual concentration by a factor of 10 while in recirculated flow through the VTE pilot plant, to determine the effects of solute concentration on the heat transfer performance. The pH of the blowdown was adjusted from 12 (as received) to 5.5 by the addition of sulfuric acid (80 ml) and 10 ppm of Neodol-25-3A (Shell Chemical Co.) was added for this test series. Deaeration of the feed was affected by recirculating it through the VTE pilot plant under vacuum. The steamside temperature of the VTE tube bundle was maintained at 220°F and the initial ΔT applied was 10°F. The condenser flux was held constant during the entire run, resulting in a gradual decrease in the ΔT to 7°F responsive to the increase in boiling point as the solute content increased. Heat transfer performance data are plotted for the 14-tube bundle of 2-inch OD double-fluted aluminum-brass tubes and for a similar copper distillation tube as a function of the residual feed volume in Figure 15 . It is interesting to note that the gradual increase in solute concentration did not have a negative effect on the overall heat transfer coefficient in this case. This is the result of the simultaneous concentration of surfactant in the residual feed and of the fact that the solubility limit of solutes was not reached during this 10-fold concentration of the blowdown. In fact a gradual increase in evaporator heat transfer performance to about 25 percent was obtained during the course of this blowdown concentration by a factor of 10. Also of interest was the fact that no excessive foaming was experienced. The final solute content of this 10-fold concentrate was about 16,500 ppm (or 1.65%) including 100 ppm of the added surfactant.

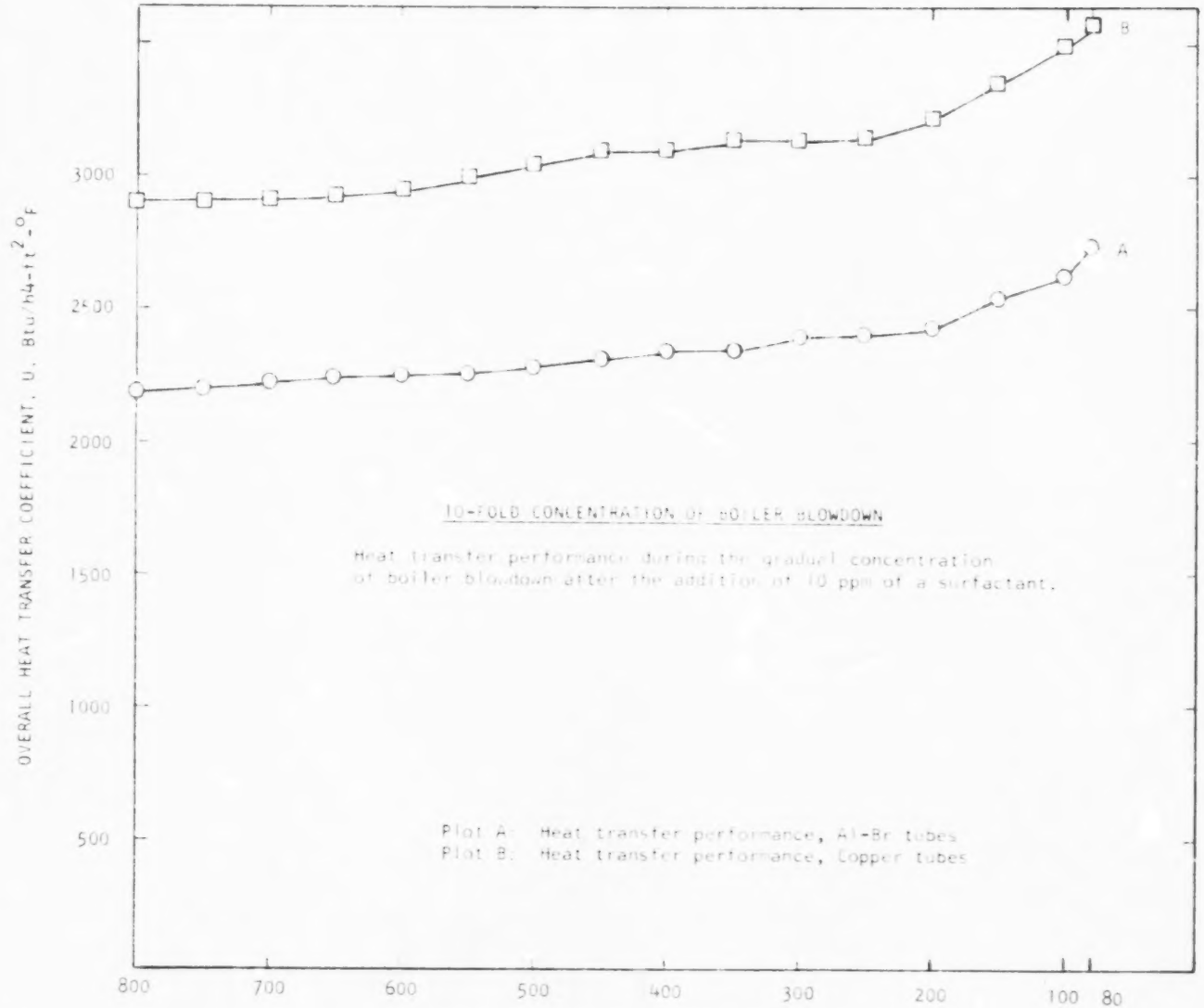

OVERALL HEAT TRANSFER COEFFICIENT, U, Btu/h4-ft²-°F
3000
2500
2000
1500
1000
500
800
700
600
500
400
300
200
100
80
RESIDUAL FEED VOLUME, GALLONS IN RECIRCULATION
B
A
10-FOLD CONLENTRATION OF BOILER BLOWDOWN
Heat transfer performance during the gradual concentration of boiler blowdown after the addition of 10 ppm of a surfactant.
Plot A: Heat transfer performance, Al-Br tubes
Plot B: Heat transfer performance, Copper tubes

FIGURE 15

(d) In a final experiment 40 liters of boiler blowdown with 10 ppm of surfactant added was concentrated in the Pyrex glass VTE of Figure 6. This concentration proceeded by a factor of 20, to a residue of 2 liters, without any significant precipitation of salts being observed. This residue was dark colored from suspended particulates, all of which were readily maintained in suspension by the presence of the surfactant additive.

Discussion. From the data plotted in Figure 13 it is apparent that the addition of about 10 ppm of surfactant to boiler blowdown evaporated at 210°F in an upflow VTE using double-fluted aluminum-brass tubes provides an approximate 120 percent increase in the evaporator performance, and an 11-fold reduction in the tubeside pressure drop. These data indicate that interface enhancement should provide substantial cost reductions in the concentration of such wastewaters. With appropriate evaporator design options, these cost reductions can be either in terms of capital cost or operation-maintenance costs.

It is clear, from a comparison of the data plotted in Figures 12 and 14, that the interface-enhanced mode of evaporation provides an approximate doubling of the upflow VTE heat transfer performance. Stated in different terms, one can increase the rate of concentration of boiler blowdown by about 100 percent by the addition of about 10 ppm of surfactant to it followed by imposing the foamy mode of two-phase flow through the upflow distillation tube under otherwise conventional process conditions.

The 10-fold concentration of boiler blowdown at 210°F without loss in heat transfer performance after the addition of 10 ppm of surfactant is considered very promising. These would essentially be the ideal VTE process

conditions for an evaporator utilizing vapor recompression as the means of supplying the process heat requirements. Vapor compression (VC) is probably the least costly method of concentrating boiler blowdown. Concentration by a factor of 20 to 25 should be readily achievable by VC-VTE with an interface-enhanced performance of about 2,000 Btu per hr-ft^2-^{o}F. Several alternative types of compressors, both electrically driven mechanical, or steam-jet types, are commercially available. The main advantage provided by interface enhancement is in this instance taken in terms of a capital cost reduction; the heat transfer surface area or number of distillation tubes used can be reduced by half.

The alternative approach of using an interface-enhanced multiple effect VTE provides the basis for saving heat or fuel costs. In this case the main advantage can be taken in terms of an improved economy ratio, by increasing the number of effects normally permissible, by about 50 percent. Economy ratios of up to 18 pounds of distillate produced per pound of heating steam are possible (6). Intermediate choices are of course possible, thus allowing flexibility for optimizing overall costs by balancing the elements of capital and operation-maintenance costs.

The beneficial side-effects of surfactant additives were also significant though not precisely defined in this case. The dispersant properties of the additive had an apparent beneficial effect of retaining particulates in suspension during the 10-and 20-fold concentrations of boiler blowdown. The heat transfer surfaces remained clean during these operations.

3) Acidic Mine Drainage Concentration

Drainage and seepage from active and abandoned mines and from slagpiles associated with such mines can present effluents that are environmentally harmful. These effluents are usually high in acidity due to atmospheric oxidation of sulfur compounds producing sulfuric acid in solution. Acidity levels in the pH-range of 2 to 4 have been reported. In addition such effluents also contain other undesirable solutes such as salts of iron, copper and zinc. Depending upon the length of atmospheric exposure, iron compounds can be present as ferrous sulfate which is gradually oxidized to ferric sulfate. The drainage water examined in this study originated from a pyrites slag pile. Two types of this effluent were examined: the first was collected directly from the slagpile before significant exposure to air oxidation and was high in ferrous content; the second type was high in ferric content, substantially fully oxidized by prolonged exposure to air and partial solar evaporation-concentration. The highly corrosive nature of these effluents presented a major operating problem. The VTE pilot was in part constructed of copper-based alloys and stainless steel, and subject to corrosive attack, especially at higher temperatures.

The experimental procedures applied can be summarized as follows:

(a) The solute behavior of these drainage waters was examined by gradual concentration in the pyrex glass VTE, to the point of precipitation of ferrous or ferric sulfate, both without and with a surfactant additive.

(b) Heat transfer performance data were obtained in the VTE pilot plant within the evaporation temperature range of 120 to 200°F. Data were obtained with copper, aluminum-brass and titanium tubes of the fluted type.

(c) The highly corrosive nature of this wastewater dictated limited use of the VTE pilot plant for its examination. Solid precipitation studies were therefore conducted with the pyrex tube exaporator. This wastewater is comparable to electroplating rinsewater, at least in terms of its metal ion content and corrosiveness. Therefore, pilot plant tests with electroplating rinsewater were also avoided.

(a.1.) The fresh ferrous-containing drainage water had a TDS of about 54,000 and a pH of 3.3. Other constituents were about 100 ppm of copper sulfate and about 150 ppm of zinc sulfate. Six liters of this were evaporated in the glass-tubed evaporator of Figure 6, at 40°C (104°F), to a residual volume of 2.0 liters, at which point a whitish crystalline precipitate started to form, at 3-fold concentration.

Eight liters of this drainage water containing 5 ppm of added Neodol-25-3A (Shell Chemical Co.) were evaporated in the glass-tubed evaporator at 90-105°F, to the onset of crystallization which occurred at a residual volume of 2.2 liters. Further crystallization occurred upon standing in this 3.6-fold concentrate.

Comment: It was apparent that the addition of a surfactant to this water (a) facilitated its evaporation by upflow VTE, and also inhibited or retarded the onset of crystallization, but did not necessarily influence the final solute concentration level in the presence of crystalline precipitates.

(a. 2.) The oxidized, ferric containing drainage water had a TDS of about 66,000 and a pH of about 2.0. Other constituents were about 120 ppm of copper and 180 ppm of zinc sulfates.

Eight liters of this water were evaporated at about 100°F in the glass-tubed evaporator to the appearance of crystalline material in the concentrate. From this 4.4-fold concentrate (1.80 liters), further crystallization occurred upon standing.

Eight liters of this water containing 5 ppm of surfactant additive (Neodol-25-3A) were concentrated at about 90°F in the glass-tubed evaporator to initial crystal formation, and then drained. This 6-fold concentrate (1.35 liters) was set aside to deposit additional crystalline material.

Comment: It was apparent that the addition of 5 ppm of a surfactant retarded crystallization and also improved upflow VTE stability and efficiency.

On a basis of these results it was decided that definitive heat transfer performance tests with the pilot plant were justifiable.

(b.1.) Heat transfer performance data obtained were limited by the corrosive nature of this acidic water. Two pilot plant runs were conducted with the 5,000 gpd VTE shown in Figure 1, using separate 80 gallon samples of the fresh, ferrous-sulfate high drainage water only.

First run: The pilot plant was tubed with 18 spiral-corrugated copper tubes of 2-inch OD x 10-foot length x 0.30-inch wall thickness (Yorkshire Imperial Metals, Ltd.) for this test.

Eighty gallons of drainage water were deaerated in the pilot plant by recirculation under vacuum (29.5-inch Hg). VTE heat transfer performance data were then taken as described earlier at evaporation temperatures of 140°, 160° and 180°F using typical multi-effect process conditions with feed flows of one gallon per minute per tube. Neodol 25-3A was then added to the feed at 10 ppm concentration, and heat transfer performance data were again taken at evaporation temperatures of 180, 160, 140 and 118°F. These data are shown in Figure 16 attached.

Comment: It was clear from the data in Figure 16 that interface enhancement provided an approximate 71 percent heat transfer performance enhancement at 180°F with 10 ppm of Neodol-25-3A additive. The two-phase pressure drop (ΔP) through the tubes was simultaneously reduced from about 39 to 8 inches of water, to improve the upflow stability and increase distillate production proportionately.

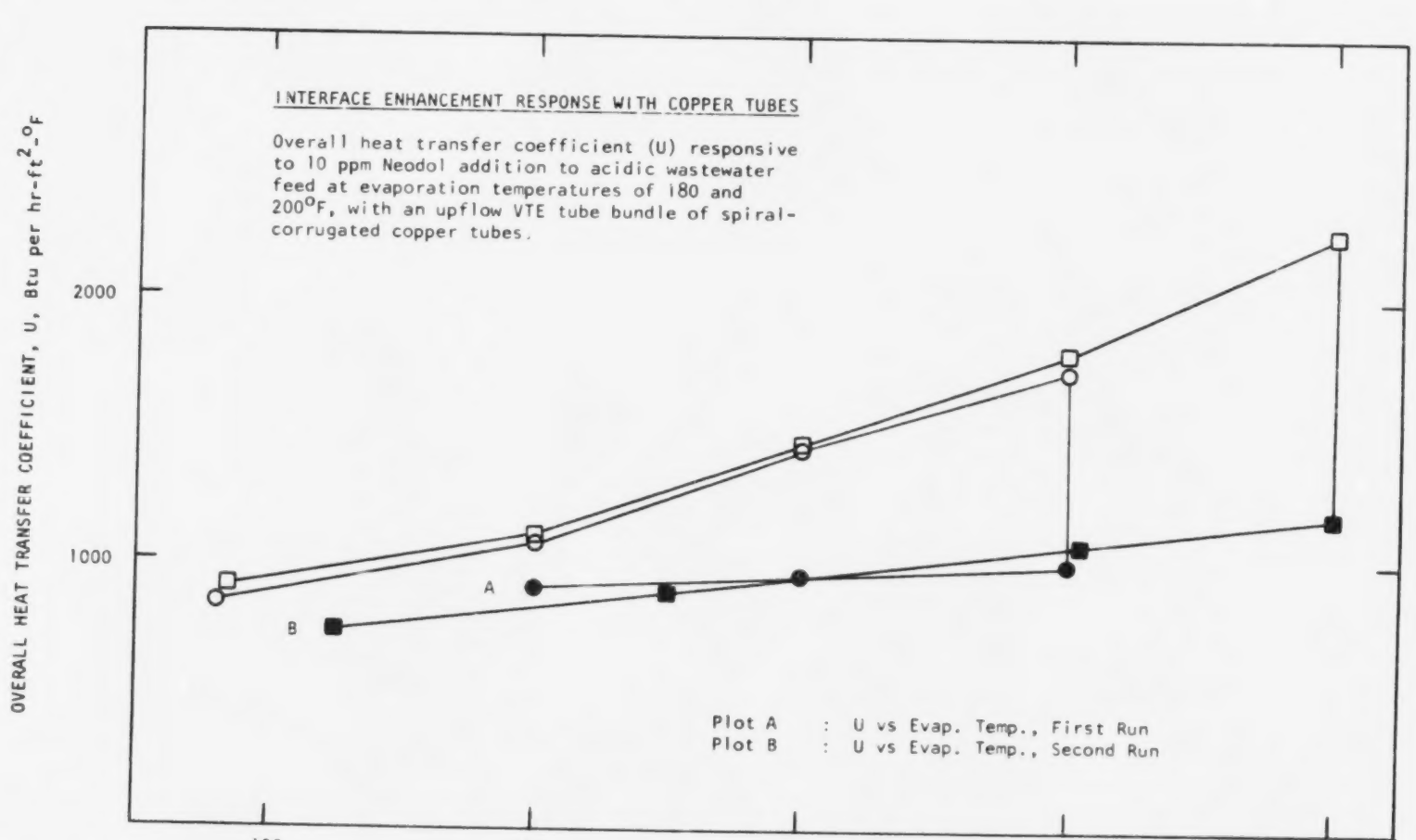

INTERFACE ENHANCEMENT RESPONSE WITH COPPER TUBES
Overall heat transfer coefficient (U) responsive to 10 ppm Neodol addition to acidic wastewater feed at evaporation temperatures of 180 and 200°F, with an upflow VTE tube bundle of spiral-corrugated copper tubes.
OVERALL HEAT TRANSFER COEFFICIENT, U, Btu per hr-ft²-°F
2000
1000
A
B
Plot A : U vs Evap. Temp., First Run
Plot B : U vs Evap. Temp., Second Run
120
140
160
180
200
EVAPORATION TEMPERATURE, °F

FIGURE 16

There was an apparent reduction in the enhancement effect of Neodol with time of the test, but this was not conclusive and it was decided to defer to a second test.

Second run: For the second run, four of the 18 distillation tubes in the bundle were replaced with a double-fluted aluminum-brass tube (Yorkshire), a spiral-corrugated titanium tube (ORNL), and two double-fluted titanium tubes (Timet-Grobb).

Eighty gallons of fresh slagpile effluent were deaerated in the pilot plant at 29.5 inch Hg, after which its pH was 3.1. Heat transfer performance data were then taken at evaporation temperatures of 125, 150, 180 and 200^{o}F as before. At 200^{o}F Neodol-25-3A was added to the feed to the 10 ppm level, and the performance data were repeated. The process conditions were then held at steady state, at 200^{o}F evaporation temperature, for 2 hours, repeating data-taking at 30 minute intervals without observing any significant reduction in the performance, thus showing that the surfactant additive is not significantly degraded by these process conditions.

Heat transfer performance data are shown in Figure 17. The aluminum-brass tubes responded best to Neodol addition; the overall heat transfer coefficient (U) increased by 100 percent, from 1302 to 2718 Btu per hr-ft^{2}-^{o}F. at 200^{o}F. The titanium tubes showed an interface enhancement response of 63 percent. The tube bundle pressure drop was reduced from 40 to 9.5 inches of water by the addition of the surfactant, comparable with the first run, and the spiral-corrugated copper tubes also responded similarly to the first run in heat transfer performance, as shown in Figure 16.

Comment: The heat transfer performance enhancement effect by Neodol addition ranges from about 60 to about 100 percent at an evaporation temperature of 200^{o}F, depending upon the type of distillation tubes used. Aluminum-

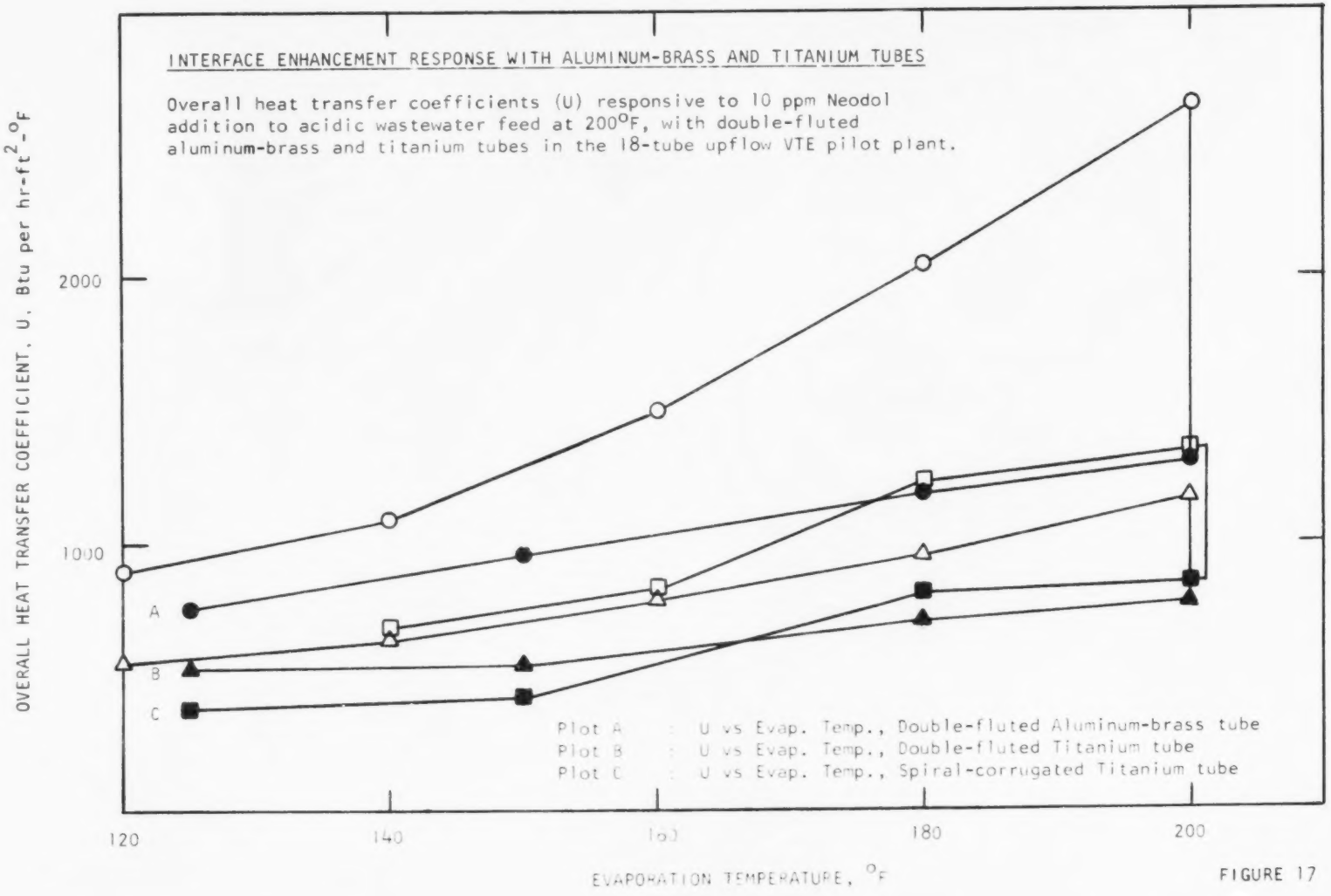

INTERFACE ENHANCEMENT RESPONSE WITH ALUMINUM-BRASS AND TITANIUM TUBES
Overall heat transfer coefficients (U) responsive to 10 ppm Neodol addition to acidic wastewater feed at 200°F, with double-fluted aluminum-brass and titanium tubes in the 18-tube upflow VTE pilot plant.
OVERALL HEAT TRANSFER COEFFICIENT, U, Btu per hr-ft²-°F
2000
1000
A
B
C
Plot A : U vs Evap. Temp., Double-fluted Aluminum-brass tube
Plot B : U vs Evap. Temp., Double-fluted Titanium tube
Plot C : U vs Evap. Temp., Spiral-corrugated Titanium tube
120
140
160
180
200
EVAPORATION TEMPERATURE, °F

FIGURE 17

brass (double-fluted) performed best, but titanium tubes will be the better choice because of corrosion-fouling problems. The double-fluted titanium tubes showed a performance enhancement of 63 percent with 10 ppm Neodol. The 4-fold pressure drop reduction by surfactant addition permitted stable upflow VTE operation at ΔT levels of 6-7^{o}F, within the range of vapor compression operation. Neodol has sufficient thermal stability at these process conditions for use as an interface enhancing agent. Considerable deposition of what appeared to be porous copper was observed at the distillation tube outlet ends. Metal surfaces were generally fouled by brownish deposits requiring repeated washing with dilute acid feed at pH_4 to remove.

DISCUSSION

Several methods of wastewater concentration are available, for the purpose of providing recycle water having a relatively low solute content and a concentrated wastewater residue for disposal. The selection of what method to use is of course dominated by their comparative economics and by the technical feasibility as it depends on the chemical properties of the wastewater. Combinations of the available concentration procedures should also be considered,in the interest of overall cost reductions. The most significant solute concentration methods are by evaporation, of which several alternative procedures are applicable: by reverse osmosis (RO), by electo dialysis (ED), by ion exchange (IE) and by precipitation techniques. Included in evaporation technologies are vertical tube evaporation (VTE) either with upflow or downflow of the feed, multistage flash evaporation (MSF) and crystallizing evaporation (CE).

The determination of the comparative economics of these concentration methods are quite complex and beyond the scope of the present study. However, recent studies conducted at the Bechtel Corporation provide a comparative cost evaluation at least for the case of cooling tower concentration-recycle; their conclusions provide a cost basis for ranking VTE with respect to other feasible alternative methods. The present study provides a basis for comparing the cost of interface-enhanced VTE with that of the conventional VTE used in the Bechtel studies. Recent design comparison studies performed by Kaiser Engineers provide a capital cost comparison of interface-enhanced VTE with conventional VTE and MSF plants of large size for sea water desalination.

The above studies by Awerbuch and Rogers (12) on the desalination of cooling tower blowdown for a large (2,200 MWE) power plant using cold lime soda softened river water for cooling, were reported in the recent EPA-AIChE sponsored Watereuse conference. A 20-fold concentrated blowdown

was considered for further concentration to a solid residue, utilizing a total of fourteen alternative procedures, and the comparative costs (capital, operating and total) were determined. Their process combinations considered, and the costs computed can be summarized as follows:

Concentration Method	Costs In $M		
	Capital	Operating	Total
1. Crystallizing evaporation	15.7	25.7	41.4
2. MSF preconcentration at 230°F maximum feed temp.; Crystallizing evaporation	9.1	20.3	29.4
3. MSF preconcentration as in 2; Vapor compression evaporation with crystal slurry recycle feed	15.8	21.2	37.0
4. MSF preconcentration at 19°F maximum feed temp; Crystallizing evaporation	7.2	17.8	25.1
5. MSF preconcentration as in 4; Vapor compression evaporation with crystal slurry recycle feed	10.9	19.4	30.3
6. Ion exchange; Reverse osmosis; Crystallizing evaporation	8.8	17.8	26.6
7. Ion exchange; Reverse osmosis; Vapor compression evaporation with crystal slurry recycle feed	21.8	23.4	45.1
8. Ion exchange; Reverse osmosis; MSF with 230°F max. temp.; Crystallizing evaporation	5.2	12.1	17.2
9. As in case 8 except using a vapor compression evaporator with crystal slurry recycle feed	7.4	12.6	20.0
10. Ion exchange; Reverse osmosis; MSF with 190°F max. temp.; Crystallizing evaporator	6.0	13.9	19.9
11. As in case 10 except using a vapor compression evaporator with crystal slurry recycle feed	8.3	14.7	23.0

Concentration Method continued	Costs In $M		
	Capital	Operating	Total
12. Hot-coolant heated upflow VTE for preconcentration; Crystallizing evaporator heated by hot coolant	8.3	11.6	19.9
13. Turbine exhaust heated upflow VTE for preconcentration; Crystallizing evaporator similarly heated	7.7	9.9	17.6
14. Downflow VTE preconcentrator and crystallizing evaporators replacing one power plant condenser, both heated with turbine exhaust steam	6.1	3.6	9.7

The least expensive method of blowdown concentration-recycle thus requires replacement of one of three typical power plant condensers with a VTE for preconcentration followed by a VTE for crystallizing-evaporation, both heated by turbine exhaust steam. This method, however, will probably require demonstration before it will be considered acceptable by the power industry since it requires a change in the established coolant cycle. Alternative method 13 appears the most acceptable from the power plant operators point of view since it requires only an addition to conventional coolant cycles. The last three and most promising of the fourteen alternative methods can be further improved, and their cost figures can be reduced by applying interface enhanced evaporation in the blowdown concentration by VTE. The emphasis in the above Bechtel study was to obtain comparative cost figures; the absolute costs may need adjustment.‡

Another alternative method of blowdown concentration recycle was recently proposed by the author (11) based on data from this study, using turbine

‡Private communication with the authors.

exhaust steam for preconcentration by interface-enhanced VTE, followed by conventional crystallizing evaporation. The main advantage of this method is that it permits the use of two evaporation effects within the temperature span available within a conventional power plant coolant cycle. This provides a basis for either producing distilled water for a beneficial purpose, such as for boiler feed or potable use, or to dilute the coolant in the main power plant coolant cycle. Since the heat transfer performance is in this case about double that of case 13 above, those cost figures would apply fairly closely here and the distillate produced would be the gain, approximately. Alternatively one could use the single-effect approach of case 13 and reduce the VTE heat transfer surface by a factor close to 50 percent. The capital cost advantage of the reduction in distillation tube requirements and the ability to use upflow VTE instead of downflow VTE provide a capital cost saving of about 25 percent for a large seawater desalting plant, according to a study by Kaiser Engineers (6). In a recent design comparison study of the interface-enhanced upflow VTE with conventional MSF for seawater desalination by Kaiser Engineers (5) it was shown that the heat transfer surface requirement of this VTE is only about half that of MSF and the evaporator vessel size is reduced by about 40 percent.

In order to arrive at realistic capital and operating cost figures for the use of interface-enhanced VTE in the concentration of cooling tower blowdown by waste heat, one would have to perform a detailed design study which was outside the scope of this work. However it is apparent that a flow diagram such as in Figure 11 should be both acceptable to power plant operation and more economical than the other alternatives considered. In the case of the most economical of the fourteen above proposed methods the use of interface enhancement will undoubtedly reduce this cost further by a significant amount.

The recommended procedure for cooling tower blowdown concentration, based on this study, is the one based on the flow diagram of Figure 11. This approach was presented at the Second National Conference on Complete Watereuse by the author in a paper titled "Recycle of Power Plant Cooling Tower Blowdown by Vertical Tube Evaporation with Interface Enhancement, Utilizing Waste Heat."

This procedure combines the advantages of minimal interference with the normal power plant operation and good economy, and it provides distilled water for boiler feed makeup or another beneficial use. This recommended procedure can be added on to a pre-existing power plant or can be designed into a new plant. Normal operation of a pre-existing power plant can be resorted to at any time, within the approximately 30 seconds required to close 4 valves through which the added-on loop interfaces with the power plant coolant cycle. The only difference between the normal, pre-existing operation and the added-on, combined operation is that the demand on the original cooling tower is reduced by about 5 percent; this is a beneficial effect, especially during hot weather conditions.

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